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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

NATIONAL DISPOSAL SITE CANDIDATE WASTE STREAM CONSTITUENT PROFILE REPORTS. PROPELLANTS, EXPLOSIVES, AND WARFARE MATERIEL

TRW Systems Group

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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY OR DISPOSAL OF HAZARDOUS WASTE

Volume VII. National Disposal Site Candidate Waste Stream Constituent Profile Reports - Propellants, Explosives, and Chemical Warfare Materiel

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REVIEW NOTICE

The Solid Waste Research Laboratory of the National Environmental Research Center - Cincinnati, U.S. Environmental Protection Agency has reviewed this report and approved its publication. Approval does not signify that the contents necessarily reflect the views and policies of this Laboratory or of the U.S. Environmental Protection Agency, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
National Environmental Research Center
Cincinnati, Ohio

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PROFILE REPORT

Bromine Pentafluoride (66)

1. GENERAL

At room temperature, bromine pentafluoride is a pale yellow liquid, normally shipped in compressed gas cylinders under its own vapor pressure. Bromine pentafluoride is a stable compound, showing no signs of decomposition up to 460 C.[1302]

Bromine pentafluoride is an extremely reactive material in that it reacts with every known element except nitrogen, oxygen, and the inert gases. Under proper conditions, it reacts with the vast majority of inorganic compounds with the exception of the inorganic fluorides. It attacks organic compounds even under mild reaction conditions.[1301]

The major use of bromine pentafluoride is as a fluorinating agent of inorganic compounds. At one time it was considered for use as a rocket propellant (oxidizer).

Bromine pentafluoride is prepared commercially, in pilot plant quantities by the direct combination of the elements at 200 C in a copper apparatus. The reaction is exothermic. The pure bromine pentafluoride is obtained by fractional distillation. The material is manufactured by Pennsalt and Allied Chemical Corporation, but at the present time there is no commercial or laboratory market; therefore, production facilities (including the former pilot plants) are not now in operation. Waste disposal procedures are necessary for handling contaminated or old liquid propellant now being stored in various DOD facilities. Total quantity stored is estimated at 1 ton or less; detailed information is not available.

2. TOXICOLOGY

The physical effects of bromine pentafluoride are considered comparable to those of chlorine trifluoride or anhydrous hydrofluoric acid. Therefore, by analogy, a maximum allowable concentration of 0.1 ppm,[1300] by volume in air for an 8-hr day is suggested. Concentrations of 50 ppm or more may be fatal in 30 min to 2 hr. In concentrations of 100 ppm, toxicity symptoms were noted after 2 min in experimental animals and at 500 ppm symptoms appeared at once.[1301]

Severe chemical burns similar to liquid fluorine burns will result if liquid bromine pentafluoride contacts the skin. The corrosiveness of bromine pentafluoride to body tissues will result in deep, painful burns which can be most serious to the eyes.

3. OTHER HAZARDS

Bromine pentafluoride is such a powerful fluorinating agent that it will react with most metal halides, will convert many oxides to fluorides and will burn with many organic compounds. Methyl chloride, for example, reacts explosively with BrF_5. Contact with water must be prevented to avoid an explosive reaction. It also must be remembered that once a fire is started, the equipment is consumed by reaction with bromine pentafluoride.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Because of the corrosive nature of bromine pentafluoride, it should be handled with extreme care. Anyone using this material should wear suitable protective clothing such as neoprene gloves, aprons and face shields. Airline or oxygen--not carbon absorbent masks--are recommended for protection against vapor only. Dry-type fire extinguishers using sodium bicarbonate can be used to treat spillage, as well as combat any secondary fires.

Bromine pentafluoride can be used with a variety of metals due to the formation of a passive metal fluoride film which protects the metal from further corrosion.[1299] Monel and nickel are preferred materials of construction; however, copper, brass and stainless steel can be used. Highly fluorinated polymers such as Teflon can be used only under static conditions with either liquid or vapor at ordinary temperature. All equipment used in bromine pentafluoride service must be thoroughly cleaned and passivated with low pressure or inert gas-diluted bromine pentafluoride before exposure to liquid or higher pressure vapors. Additional details for the safe handling, transportation and storage of bromine pentafluoride are described in Allied Chemical Technical Bulletin TA-8532-3.[1302] This document provides recommended procedures for equipment design, employee safety, design of shipping and storage containers, tank and equipment cleaning and passivation procedures, emergency rescue, first aid and material specifications.

Bromine pentafluoride is shipped under Department of Transportation (DOT) and U.S. Coast Guard regulations in cylinders approved for shipment of compressed gases. It is shipped as a corrosive liquid, taking a White Acid Label.

The safe disposal of bromine pentafluoride is defined in terms of the recommended provisional limits in the atmosphere, and in potable water sources. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Bromine pentafluoride	.007 mg/M^3	.01 x TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Bromine Pentafluoride	Reacts quantitatively with water	

Disposal/Reuse

A definition of acceptable criteria for the disposal of bromine pentafluoride must also take into account acceptable criteria for the release or treatment of compounds formed during treatment of bromine pentafluoride. Compounds formed by the treatment methods normally used and their disposition are as follows:

Compounds Formed	Disposition
Bromine	Condense/recover
Chlorine	Condense/recover/Scrub
Sodium Fluoride	Treat with a soluble calcium salt and deposit the resultant calcium fluoride with that collected from treatment of other fluorides
Carbon Tetrafluoride	Vent

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Manufacturers of interhalogen compounds do not discharge waste streams of these compounds, but instead discharge any excess or contaminated interhalogen compounds into the reactors currently used to manufacture fluorine compounds.[1304] There are no published methods in the unclassified literature describing the disposal of bromine pentafluoride except by venting in a remote area which is not considered satisfactory. The possible disposal methods are described below. It should be noted that these methods have been employed on a laboratory scale only and that engineering design data is almost completely lacking.

Option No.1 - Conversion to Sodium Fluoride, Chlorine and Bromine

Bromine pentafluoride diluted to less than 50 mole percent with nitrogen can be quantitatively converted to sodium fluoride, chlorine and bromine by passage through a reactor tube filled with approximately 100 mesh sodium chloride.[1304] Nitrogen or helium is required as a carrier because bromine pentafluoride has a vapor pressure of approximately 7 psia at 72 F. The bromine can be condensed in a trap cooled with ice water while the chlorine can subsequently be converted to NaOCl by absorption in a sodium hydroxide solution. The NaOCl produced can be used in the treatment of other wastes at the National Disposal Sites. The collected bromine can be purified by distillation and recovered. Techniques similar to this have been used by TRW for disposal of other interhalogen compounds.

The sodium fluoride produced is allowed to accumulate in the NaCl bed until the reactivity of the bed reaches an undesirably low level. At that time, the NaF is disposed of by reaction in solution with lime, as per the Profile Report on Sodium Fluoride (389).

Option No.2 - Reaction with Charcoal

The classic fluorine disposal unit is a charcoal bed composed of 3/8-in charcoal bits,[1154] and this method has been used with BrF_5 and other interhalogen compounds.[1300,1304] The products for bromine pentafluoride are carbon tetrafluoride and bromine with the conversion believed to be quantitative. Carbon tetrafluoride is chemically inert and relatively non-toxic,[1303] and is therefore vented. Bromine is collected in a trap cooled with ice water. If large quantities of bromine pentafluoride are to be treated in this manner, the charcoal reactor will become a huge furnace. The charcoal disposal system has proven successful for quantities of fluorine up to 30 lb in approximately 3 min (600 lb per hour).[1154] Continuous operation requires a number of parallel disposal reactors. Approximately 17 lb of charcoal are required to treat 100 lb of fluorine. No thorough evaluation of the charcoal reactor has been made for bromine pentafluoride.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is suggested that National Disposal Sites have a unit operation capable of handling fluorine and the interhalogen compounds. The unit should be a charcoal reactor and contain options for treating each of these compounds. It is recommended that a development investigation be conducted to provide engineering data for the design of a disposal unit. Since bromine pentafluoride and other interhalogen compounds are usually stored in DOT approved cylinders, shipment of bromine pentafluoride to a National Disposal Site should not present any problems, and is viewed as permissible.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Bromine Pentafluoride (66)

IUC Name Bromine Pentafluoride

Common Names

Structural Formula

BrF_5

Molecular Wt. 174.92 Melting Pt. -61.3 C (1) Boiling Pt. 40.5 C (1)

Density (Condensed) 2.57 @ 0 C Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

362 Torr @ 22 C @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Explodes Hot Water Ethanol Reacts Violently

Others:

Acid, Base Properties In water, a strong acid because of liberation of HF.

Highly Reactive with All organic materials; explodes with water unless in a dilute stream reacted with a spray (1)

Compatible with Stainless steel; monel; quartz when dry (1)

Shipped in

ICC Classification White label corrosive liquid(2) Coast Guard Classification

Comments Fumes in air; decomposes at 469 C

References (1)

(2)

PROFILE REPORT

Chlorine Trifluoride and Chlorine Pentafluoride (106)

1. GENERAL

Chemical Week, Buyer's Guide Issue [1411] indicates that chlorine trifluoride is manufactured by four companies in tonnage quantities--Air Products and Chemicals, Inc., Allied Chemical Corporation, Harshaw Chemical Company, and Union Carbide. Chlorine pentafluoride is, however, not presently in production and only limited quantities (less than 1 ton) are stored in liquid propellant test facilities throughout the country.

Chlorine trifluoride is nearly colorless as a vapor. The liquid is clear and faintly greenish-yellow in color. Its odor has been described as both sweetish and pungent, similar to chlorine or mustard gas. It is a toxic oxidizing agent similar to elemental fluorine in reactivity. It is hypergolic with most fuels, the liquid being more reactive than the gas.

Chlorine pentafluoride vapor is colorless. The liquid is clear with a very slight greenish cast. It is a toxic and corrosive oxidizing agent similar to elemental fluorine in reactivity and is chemically quite similar to chlorine trifluoride.[1300] Much of the literature concerning chlorine pentafluoride is classified. Both chlorine trifluoride and pentafluoride are easily liquified at low pressures at atmospheric temperatures which makes them attractive as rocket propellant oxidizers in place of cyrogenic liquid fluorine. Chlorine trifluoride has found limited use as a fluorinating agent under controlled conditions and for cutting metals such as oil well casings.[1301,1302] Chlorine pentafluoride has no use other than as a propellant. The physical/chemical properties for these compounds are summarized in the attached worksheets.

2. TOXICOLOGY

Exposure to chlorine trifluoride and chlorine pentafluoride vapor can cause severe irritation of the eyes, mucous membranes and the entire respiratory tract. Exposure to high concentrations may result in acute respiratory distress, pulmonary edema, and death. For most individuals the odor of these compounds is objectionable well before the emergency exposure level is reached but in some cases not before the threshold limit is reached.[1300]

The Threshold Limit Value (TLV) for chlorine trifluoride is 0.1 ppm (ACGIH 1969). No TLV has been established for chlorine pentafluoride but the TLV should probably be the same as for chlorine trifluoride.

The following emergency exposure limits have been established:

Chlorine trifluoride

10 min at 7 ppm
30 min at 3 ppm
60 min at 1 ppm

Chlorine pentafluoride

10 min at 3.0 ppm*
30 min at 1.5 ppm*
60 min at 0.5 ppm*

Contact with the skin requires an immediate drenching shower with continued, copious quantities of water, and prompt removal of clothing. The areas of exposure should be flushed with a 2 to 3 percent aqueous ammonia solution, followed by fresh water rinses. Ice cold saturated magnesium sulfate or 70 percent isopropanol (iced) should be kept in contact with the exposed area following this for at least 30 min. A paste of MgO and glycerin should then be applied.[1301]

---

* Tentative

Eyes which have been exposed to ClF_3 or ClF_5 should be irrigated with clean water for at least 15 min., with the eyelids held apart. A physician should be called immediately. No oils or oily ointments should be used.[1301]

Individuals who have been exposed to gaseous ClF_3 or ClF_5 should be carried into a clean atmosphere at once. Oxygen administration should be started immediately. A physician should be called immediately. 24 hours should be allowed to elapse before the exposed individual returns to normal employment even in the absence of symptoms.[1301]

3. OTHER HAZARDS

Both compounds are hypergolic with most materials. Both react violently with small quantities or pools of water, but with a water spray or copious amounts of water they react smoothly forming hydrogen fluoride and chlorine as major products of the reaction. Both compounds react strongly with silicon-containing compounds and support combustion of sand, asbestos, and ground glass. They react with most metals and metal oxides at elevated temperatures. The amount of heating varies with the materials. "Hot spots" developed from a trace of combustible materials or by a compression wave or friction such as closing a valve may be a source of ignition [1300] in piping systems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Because of the extremely corrosive and toxic character of both chlorine fluorides, personnel must wear appropriate protective clothing when handling equipment which contains (or contained) the fluorides. As a minimum, this should include rubber gloves, safety glasses, a face shield, and a protective apron. All work should be done in a well-ventilated area.[1301]

Flow control from cylinders should be by means of a clean passivated needle valve, fabricated from the permissible materials of construction. Traps, check valves, or vacuum breaks must be used to prevent suckback.[1301]

A quick trip, instant acting safety shower must be available, as should buckets filled with dry $NaHCO_3$ to absorb spillage. An air-line respirator or oxygen mask must be available, in an area not subject to contamination.[1301]

Storage cylinders should never be dropped or allowed violent impact. A definite area should be assigned for storage; the area should be dry, cool, and well-ventilated. Construction of the storage area should be of fire-resistant materials. Cylinders must be protected from excessive temperatures, and should be protected against the extremes of weather, and shielded from direct sunlight.

Valve protection caps should be left in place until the cylinder is secured. Cylinders should be moved by hand truck only.[1301]

The preferred materials of construction are monel and nickel; because of the formation of passive metal fluoride films, copper, brass, and steel alloy can also be used. Gaskets for flow use should be soft copper, lead, or Teflon impregnated with calcium fluoride. Valve packings should be braided copper backed with Teflon.[1301]

All equipment used in chlorine fluoride service must be thoroughly cleaned. It is mandatory that all contaminants (grease, pipe dope, scale, oil, and other contaminants) be completely removed by mechanical and chemical cleaning and solvent degreasing. The system should be completely dry before use. After cleaning, the system should be passivated by contact with a dilute mixture of chlorine fluoride in dry oil-free nitrogen gas prior to use in chlorine fluoride service.[1301]

Detailed procedures for safe handling, transportation, and storage are available in the JANAF publication on liquid propellants,[1300] and in the USAF specifications for the chlorine fluorides.[1412,1413] Crews handling the materials must be familiar with the pertinent detailed procedures.

Both compounds are shipped in 1-ton cylinders as a corrosive liquid taking a "White Acid Label." Only chlorine trifloride can be shipped by common carrier.

Disposal/Reuse

If the disposal of either of these compounds is necessary at the manufacturing site, the compound is discharged into a reactor preparing another fluoride compound.[1304] However, if disposal is to be accomplished at another site, the definition of acceptable criteria for disposal of these compounds must also take into account acceptable criteria for release or treatment of compounds formed during their treatment. Compounds formed by the described treatment methods and their disposition are as follows:

Compound	Disposition
Chlorine	Scrub with caustic solution (See Profile Report on Chlorine [105])
Hydrogen chloride	Scrub with caustic solution (See Profile Report on Hydrogen Chloride [217])
Hydrogen fluoride	Treat with lime or limestone. Place calcium fluoride formed in land field (See Profile Report on Hydrofluoric Acid [216])
Carbon Tetrafluoride	Vent

Safe disposal of the chlorine fluorides is defined in terms of the following recommended provisional limits in the atmosphere, in potable water sources, and in marine habitats:

Contaminant in Air	Provisional Limit	Basis for Recommendation
ClF_3	0.001 ppm	.01 TLV
ClF_5	0.001* ppm	.01 TLV*
Cl_2	0.01 ppm	.01 TLV
HCl	0.05 ppm	.01 TLV
HF	0.03 ppm	.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
ClF_3 ClF_5	React quantitatively with water, to yield the products listed below:	
Cl_2	0.15 ppm	Stokinger and Woodward method
HCl	0.35 ppm	
HF	0.02 ppm	

Wastes containing the chlorine fluorides will most probably be in the form of the pure materials, where disposal is required for surplus or aged propellant stored at such federal facilities as Edwards AFB, California or China Lake NWTS, California.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Detailed discussions of the possible disposal methods are described below:

Option No. 1 - Venting

Disposal of these compounds is accomplished in an isolated, posted area by remotely controlled dumping through a pipe to a shallow evaporating pan where the material is allowed to evaporate[1300]; however, this is not considered a satisfactory disposal method.

Option No. 2 - Reaction with a Charcoal Bed

The classic fluorine disposal unit is a charcoal bed, composed of 3/8-in. charcoal bits.[1154] This method has been used with other interhalogen compounds.[1300,1304] The products are carbon tetrafluoride and chlorine. Carbon tetrafluoride is chemically inert and relatively non-toxic, [1141] and, therefore, is vented. Chlorine produced is removed by a caustic scrubber. Amorphous carbon and charcoal are highly hypergolic with fluorine and react smoothly at all conditions, even at very low fluorine concentrations such as 0.3 percent.[1154] At TRW, similar results were obtained in reacting charcoal with chlorine trifluoride and pentafluoride. If large quantities of chlorine trifluoride or pentafluoride are to be treated in this manner, the charcoal reactor will become a huge furnace. However, the charcoal disposal system has proven successful for quantities up to 30 lb of fluorine in approximately 3 min. (600 lb per hour). Continuous operation requires a number of parallel disposal reactors. Approximately 17 lb of charcoal is required to treat 100 lb of fluorine. Engineering data similar to that obtained for fluorine has not been obtained for chlorine trifluoride and pentafluoride, but is required to adequately design a charcoal reactor for these two interhalogen compounds.

Option No. 3 - Propane Burner

The use of a propane burner similar to those used for disposal of difluoride is the third option.[1414] The unit consists of a burner, stack, propane supply and control system, and an air blower. The fluorine compound is discharged into the burner, which is run rich in propane. Both hydrogen fluoride and chloride are formed as reaction products and require scrubbing. Such a unit should be satisfactory for large quantities of the two compounds.

Option No. 4 - Discharge into Water Spray

These compounds have been destroyed by discharging into a large volume water spray.[1304] The resulting hypochlorous, hydrochloric and hydrofluoric acids were then treated with lime. This method is satisfactory for destroying large and small quantities of the two compounds.

Option No. 5 - Reaction with Sodium Chloride

Vapors of chlorine trifluoride or pentafluoride can be passed through a reactor tube filled with sodium chloride which converts either compound to chlorine.[1304] The chlorine produced can be recovered or absorbed by a caustic scrubber. This method, though satisfactory, offers no advantage over Options 2, 3, and 4.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is recommended that National Disposal Sites have a unit operation capable of handling fluorine, interhalogen compounds, and chlorine. Since this unit operation will not be required to handle large volumes of these compounds, the unit can contain options for treating each of these compounds. It is suggested that experimentation be conducted to generate the necessary engineering data for construction of such a unit.

Options 2, 3, 4, and 5, listed in order of desirability, are all satisfactory for disposing of chlorine trifluoride and pentafluoride, but Option 2, Reaction with a Charcoal Bed, is recommended for use at a National Disposal Site. This method is recommended because it can be used with both the interhalogen compounds and fluorine. This method has been evaluated thoroughly for fluorine and has been used extensively in the laboratory for disposing of the interhalogens.

Both chlorine trifluoride and pentafluoride are usually stored in steel tanks approved by the U.S. Department of Transportation (DOT) for shipment of the two compounds. Therefore, transportation of these compounds to a National Disposal Site can be accomplished with ease.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chlorine Trifluoride (106)

IUC Name Chlorine Trifluoride

Common Names

Structural Formula

$Cl\,F_3$

Molecular Wt. 92.46 Melting Pt. -76.32 C Boiling Pt. 11.75 C

Density (Condensed) 1.825 g/cc @ 20 C Density (gas) 0.0040 g/cc @ 12 C

Vapor Pressure (recommended 55 C and 20 C)

20.06 torr @ -46.97 C 185.01 ton @ -17.63 503.67 @ 2.37 C

Flash Point -

Autoignition Temp. -

Flammability Limits in Air (wt %) Lower none Upper

Explosive Limits in Air (wt. %) Lower Upper

Critical Temperature 426.7 K

Solubility

Cold Water Reacts violently Hot Water Reacts violently Ethanol Reacts violently

Others:

Acid, Base Properties In water, forms HF, HOCl and HCl, strong acids

Highly Reactive with most oxidizable substances at room temperature; with H_2O to give HF, O_2, Cl_2, OF_2; with most metals at high temperature.

Compatible with copper, brass, steel, nickel

Shipped in steel cylinders

ICC Classification White label corrosive liquid Coast Guard Classification Not permitted on passenger vessels

Comments

References (1) 1302

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Chlorine Pentafluoride (106)

IUC Name Chlorine Pentafluoride

Common Names

Structural Formula

$Cl\ F_5$

Molecular Wt. 130.46 Melting Pt. -103 C Boiling Pt. -13.1 C

Density (Condensed) 1.9 g/cc @ -13.1 C Density (gas) 4.5 @ 20 C

Vapor Pressure (recommended 55 C and 20 C)

2.44 psia @ -58 F 8.85 psia @ -13 F 58.76 psia @ 77 F

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Reacts violently Hot Water Reacts violently Ethanol Reacts violently

Others:

Acid, Base Properties In water, forms HF, HOCl and HCl, strong acids

Highly Reactive with all organics and most metals when heated

Compatible with copper, monel

Shipped in steel cylinders

ICC Classification White label corrosive liquid Coast Guard Classification Not permitted on passenger vessels

Comments

References (1) 1300

PROFILE REPORT

Diborane, Tetraborane, Pentaborane-9, Pentaborane-11, Hexaborane and Decaborane(61,505)

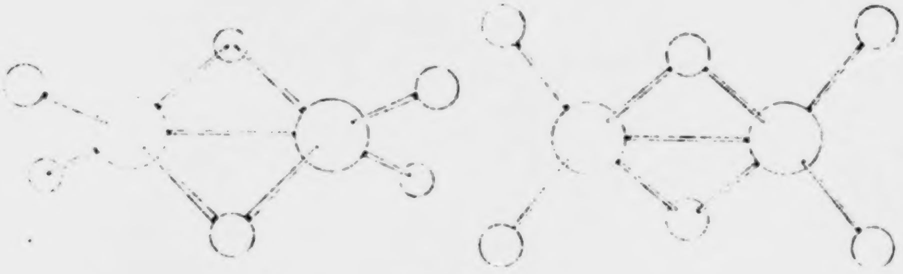
1. GENERAL

Structure and Nomenclature

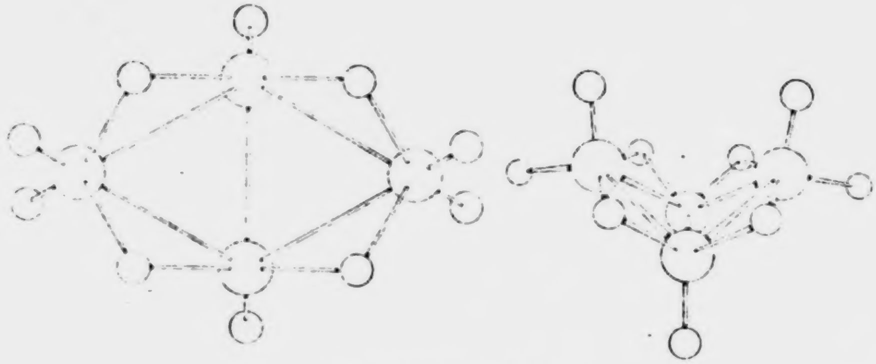
The boranes (boron hydrides) are compounds of boron and hydrogen. The boron atoms are bonded to each other directly and also by means of hydrogen atoms which form bridges between them by means of hydrogen-bonding. Their chemical properties and reactions are well-documented in several comprehensive reviews.[1433,2005,2009,2014,2002] Representative structures have been delineated (Figure 1).[1433] The monomer exists only transistorily. For the boranes which are relatively stable, the number of boron atoms in the compound is denoted by a Greek prefix, e.g., diborane for B_2H_6, tetraborane for B_4H_{10}, etc. If there may be some ambiguity with respect to the number of hydrogen atoms involved, that number is specified in parentheses, e.g., pentaborane (9) for B_5H_9 and pentaborane (11) for B_5H_{11}.

Production

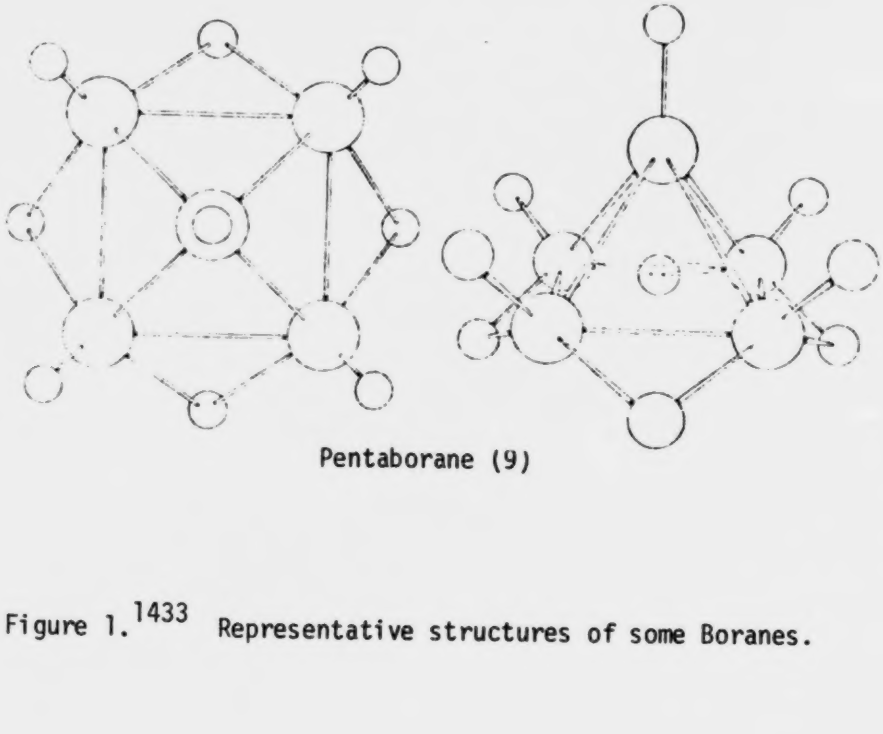
There is only one producer of boranes in the United States, the Callery Chemical Company, Callery, Pennsylvania.[2020] By 1962, Callery had produced 500,000 lb of assorted boranes under government contract for research in rocket fuels. Of this quantity, approximately 200,000 lb of pentaborane (9) remains in storage at Edwards Air Force Base, California, in the Mojave Desert. None is being produced for this purpose at present, nor is any future need anticipated, since its extreme toxicity and thermodynamic properties make it unfavorable with respect to F_2-H_2, F_2-O_2 and other newer formulations.[2019,2020]



Diborane

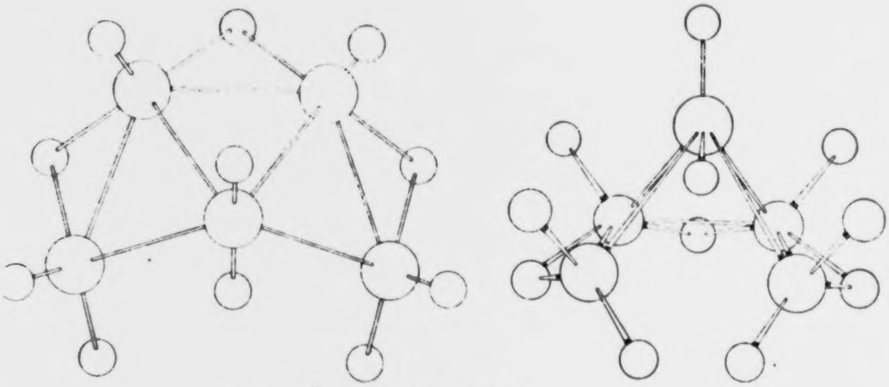


Tetraborane (10)

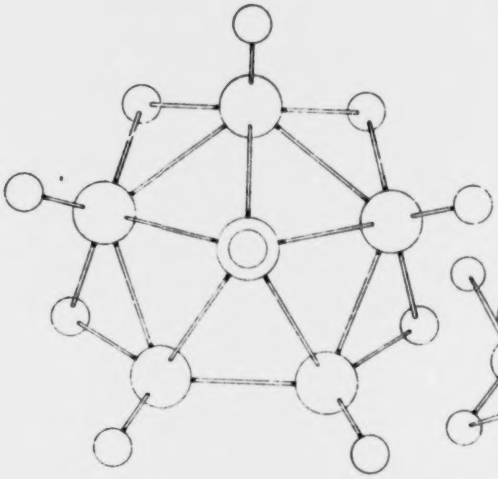


Pentaborane (9)

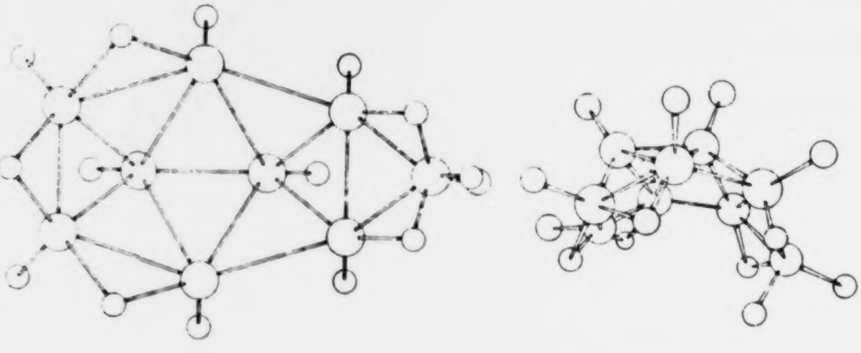
Figure 1.[1433] Representative structures of some Boranes.



Pentaborane (11)



Hexaborane(10)



Nonaborane (15)

Figure 1. (Continued)

Only diborane and decaborane are manufactured at present. There are several viable processes for producing diborane, either commercially or on a laboratory scale (e.g., Figures 2 - 4).[2092] At present, Callery produces diborane only at its Callery, Pennsylvania facility by reacting sodium hydride with methylborate according to the following reactions[2092,2020]:

$$1)\quad H_3BO_3 + 4CH_3OH \xrightarrow{\text{distillation}} CH_3OH\cdot(CH_3O)_3B + 3H_2O \quad \text{Yield} = 98\%$$

$$2)\quad CH_3OH\cdot(CH_3O)_3B \xrightarrow{\text{Mineral oil extraction}} (CH_3O)_3B + CH_3OH \quad \text{Yield} = 96\%$$

$$3)\quad 2(CH_3O)B + NaH \xrightarrow{\text{in mineral oil}} (OCH_3)_2BH + NaB(OCH_3)_4 \quad \text{Yield} = 94\%$$

$$4)\quad 6(CH_3O)_2\,BH \xrightarrow{\text{straight disproportionation}} B_2H_6 + 4(CH_3O)_3B \quad \text{Yield} = 100\%$$

There is essentially no toxic waste generated by the process. Although the producers would not release a production figure, an unidentified source estimated an annual production of <200 lb, which is almost all sold as a 10 mole per cent mixture in either argon, nitrogen or hydrogen at $85/lb contained B_2H_6.

Decaborane is produced by pyrolysis of diborane. Miscellaneous toxic wastes are separated and incinerated. The stack gases are neither monitored nor controlled. Decaborane is of some research interest as a component of solid propellants, and the exact amount produced is classified by the Department of Defense. At $1000/lb, however, it is doubtful if much is produced.

Tetraborane, pentaborane (11), and hexaborane are highly unstable laboratory curiosities which are produced locally in individual research laboratories in negligible quantities. They rapidly transform to the other boranes with the evolution of hydrogen.

Uses

Diborane is used almost exclusively for defect doping in the manufacture of semiconductors. Three major gas suppliers, Matheson Gas Products, Cucamonga, California[2011] and Newark, California,[2010] Air Products and Chemicals Inc., Long Beach, California[2015] and Emmaus, Pennsylvania,[2017] and the Linde Division, Union Carbide Corporation,

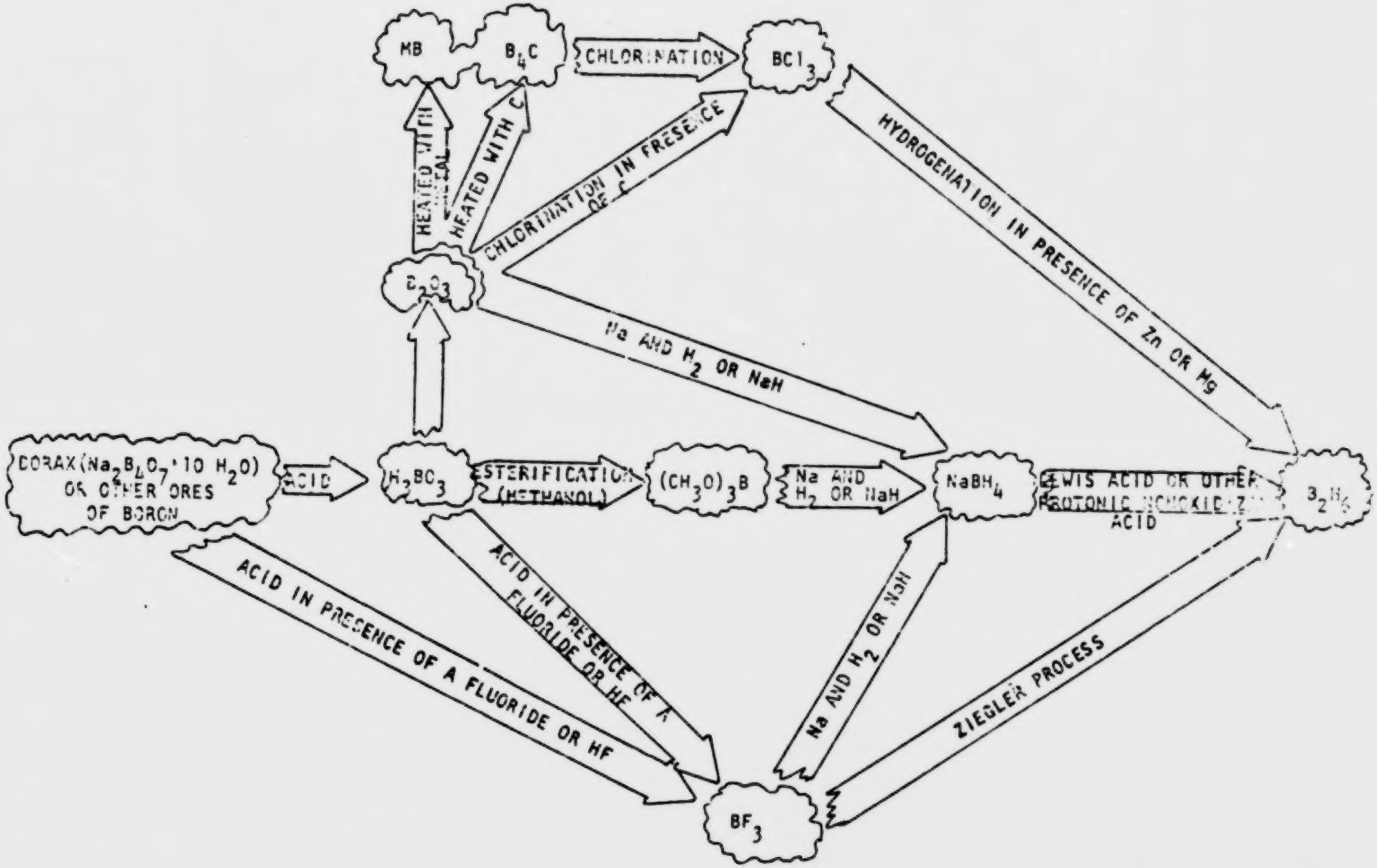

BORAX (Na₂B₄O₇·10 H₂O) OR OTHER ORES OF BORON
ACID
H₃BO₃
B₂O₃
MB
B₄C
HEATED WITH METAL
HEATED WITH C
CHLORINATION
BCl₃
CHLORINATION IN PRESENCE OF C
Na AND H₂ OR NaH
ESTERIFICATION (METHANOL)
(CH₃O)₃B
Na AND H₂ OR NaH
NaBH₄
LEWIS ACID OR OTHER PROTONIC [illegible] ACID
B₂H₆
HYDROGENATION IN PRESENCE OF Zn OR Mg
ACID IN PRESENCE OF A FLUORIDE OR HF
ACID IN PRESENCE OF A FLUORIDE OR HF
Na AND H₂ OR NaH
ZIEGLER PROCESS
BF₃

Figure 2.[2092] Flow Chart for the Preparation of Diborane via the Conversion of Boron Ores Into Boron Halides or Sodium Borohydride.

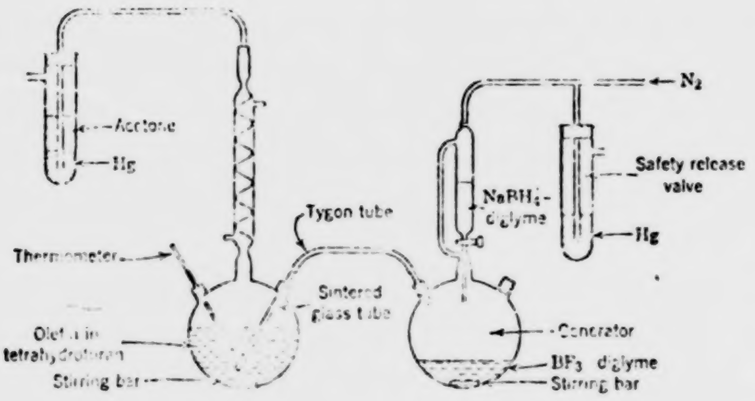

Acetone
Hg
Tygon tube
Thermometer
Sintered glass tube
Olefin in tetrahydrofuran
Stirring bar
N_2
Safety release valve
NaBH$_4$-diglyme
Hg
Generator
BF$_3$ diglyme
Stirring bar

Figure 3. Laboratory Method for the Preparation of Diborane[2092]

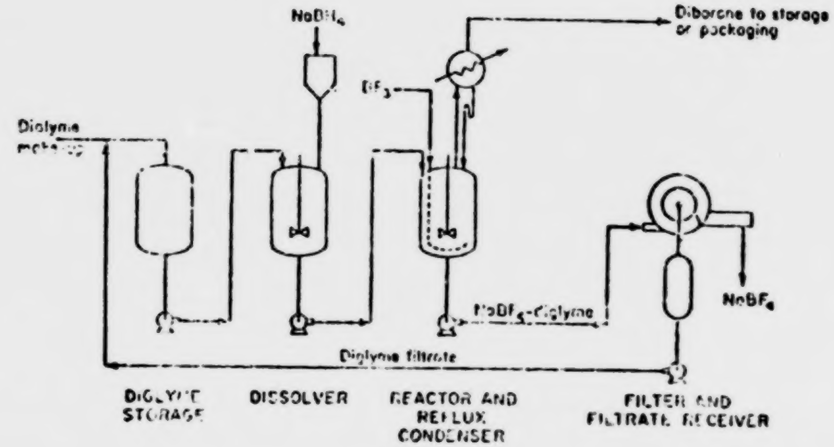

NaBH$_4$
Diborane to storage or packaging
BF$_3$
Diglyme makeup
NaBF$_4$
NaBF$_4$-Diglyme
Diglyme filtrate
DIGLYME STORAGE
DISSOLVER
REACTOR AND REFLUX CONDENSER
FILTER AND FILTRATE RECEIVER

Figure 4. Flow Diagram for the Commercial Manufacture of Diborane by the $NaBH_4$-BF_3-Diglyme Process[2092]

Torrance, California,[2018] buy 10 mole percent B_2H_6 mixed with either argon, nitrogen, or hydrogen at $85/lb contained B_2H_6, further dilute it to various concentrations from 10 ppm to 1000 ppm (but most typically 100 ppm), and resell it to the semiconductor manufacturers, who use it to introduce defects in the assembly line production of semiconductors, at temperatures ranging from moderate to 1100 C. Two manufacturers, TRW Semiconductors, Lawndale, California[2016] and Collins Radio Company, Newport Beach, California[2012] report annual use of 10 and 6 standard 240 ft^3 cylinders of diluted gas, respectively.

Aside from a small amount of decaborane used in classified research in solid propellants, 20 to 30 kg/yr are used by the Olin Corporation, New Haven, Connecticut, in the manufacture of Dexsil, a patented, polysilicone, high temperature elastomer.[2008] The decaborane is obtained at present from a large stockpile which is the property of Olin. Since the material is very valuable at $1000/lb on the open market, all waste is recycled and none escapes. The stockpile is stored at cryogenic temperatures and is continuously monitored for the evolution of hydrogen, which would signal that decomposition is occurring.

On the West Coast, Chemical Systems, Inc., Santa Ana, California,[2006] manufactures Pentasil, which is similar to Dexsil, but uses pentaborane instead. They use 50 to 75 lb/yr of pentaborane, which they obtain from the stockpile at Edwards Air Force Base, California. Their only waste product is hydrogen, which is vented. Occasionally, they experiment with diborane, which is reacted completely with acetylene in a bomb to produce boron carbide and hydrogen.

Sources and Types of Borane Wastes

The types and sources of borane wastes include (Table 1): (1) residual gas left in manifolds when the 10 mole percent diborane is diluted to various concentrations by Air Products and Chemicals, Linde, and Matheson; (2) decaborane containing gases released to the atmosphere in the burning of solid wastes generated in decaborane manufacture by Callery Chemical Company; and (3) the 200,000 lb pentaborane stored in gas cylinders at the Edwards Air Force Base in California.

TABLE 1

BORANE WASTES

Material	Industry	Process	Quantity and Waste Form	Geographical Distribution
Diborane	gas-mixing	dilution with argon, nitrogen, or hydrogen for resale	<0.1 ft^3/plant-month as residual gas in manifolds	Air Products and Chemicals, Inc. - Emmaus, Pennsylvania; Long Beach, California; and Houston, Texas Linde Division of Union Carbide Corp. - East Chicago, Indiana; Houston, Texas; Keasely, New Jersey; Linden, New Jersey; and Torrance, California Matheson Gas Products, Inc. - Cucamonga, California; Newark, California; and East Rutherford, New Jersey
Decaborane	chemical	incineration	several lb solid/yr incinerated; toxic gases released to the atmosphere	Callery Chemical Company - Callery, Pennsylvania
Pentaborane	U. S. Air Force	storage	200,000 lb stored in gas cylinders	Edwards Air Force Base, California

2. TOXICOLOGY[0766,0648,2000,1312,2092]

Health and Safety Standards

Recommended Threshold Limit Values (TLV) have been established by the American Conference of Governmental Industrial Hygienists for diborane, pentaborane (9), and decaborane, as follows:

	Threshold Limit Value	Minimum Level Detectable by Odor by Man[648]
Diborane	0.1 ppm (100μg/m^3)	3.3 ppm (33,000μg/m^3)
Pentaborane	0.005 ppm (10μg/m^3)	0.8 ppm (1,600μg/m^3)
Decaborane	0.05 ppm (300μg/m^3)	0.7 ppm (4,200μg/m^3)

It is seen that the minimum concentrations detectable by odor are much higher than the maximum set for reasons of health. Consequently, odor may not be relied upon as a means of detection. While several instruments are available for the detection of boranes in the sub-parts per million range,[2092] they are of limited utility due to non-portability and/or non-specificity. Detection remains as an outstanding problem.

The Committee on Toxicology of the National Research Council has established Emergency Exposure Limits (EEL) for diborane as 10 ppm for 10 minutes, 5 ppm for 30 minutes, and 2 ppm for 60 minutes.[2092] These are not safety limits, but rather predictions for the onset of clinical symptoms without incapacitation. Similarly, an EEL of 25 ppm for 5 minutes has been set by the American Industrial Hygiene Association for pentaborane.[0648]

Epidemiology

Accidents involving human exposure to boranes have primarily involved inhalation and subsequent lung irritation and pulmonary edema. Attack of the central nervous system has been inferred by accompanying listlessness, incoordination, and similar symptoms. This clinical evidence has been supplemented by laboratory experiments with dogs and rats, which have produced liver and kidney damage in addition.[0766,0648] It has not been determined whether the effects of borane poisoning are cumulative in animals or man. The 1971 Annual List of Toxic Substances[1312] reports 50th percentile lethal doses or lethal concentrations (LD50 or LC50) as:

Diborane	80 ppm LC50 in the rat by inhalation.
Pentaborane	0.72 mg/kg LD50 in man by inhalation.
	7 ppm LD50 in the rat by inhalation
	11.1 mg/kg LD50 in the rat administered intraperitoneally.
Decaborane	230 mg/m^3 LC50 in the rat by inhalation
	64 mg/m^3 LD50 in the rat administered orally.

3. OTHER HAZARDS

Pure boranes are stable. However, small quantities of wide varieties of impurities, particularly oxidizing substances, water, or halogenated hydrocarbons, renders them extremely unstable with respect to thermal or mechanical shock.[2092,2000] This could account for wide discrepancies in experimental results on the pyrophoricity of diborane. It must always be assumed in the absence of a great preponderance of evidence to the contrary that a borane cylinder is so contaminated. The problem is compounded by the likely evolution of hydrogen gas on reaction, decomposition or polymerization, or testing. The hydrogen, itself, is of course, highly explosive, and can cause cylinders to burst by pressure build-up. At slightly elevated temperatures, diborane will decompose (or polymerize) to release varying amounts of hydrogen. Alternatively, the high polymers will decompose, also releasing hydrogen. Some of the rates of the reactions have been investigated as a function of time and temperature (Figure 5).[1414]

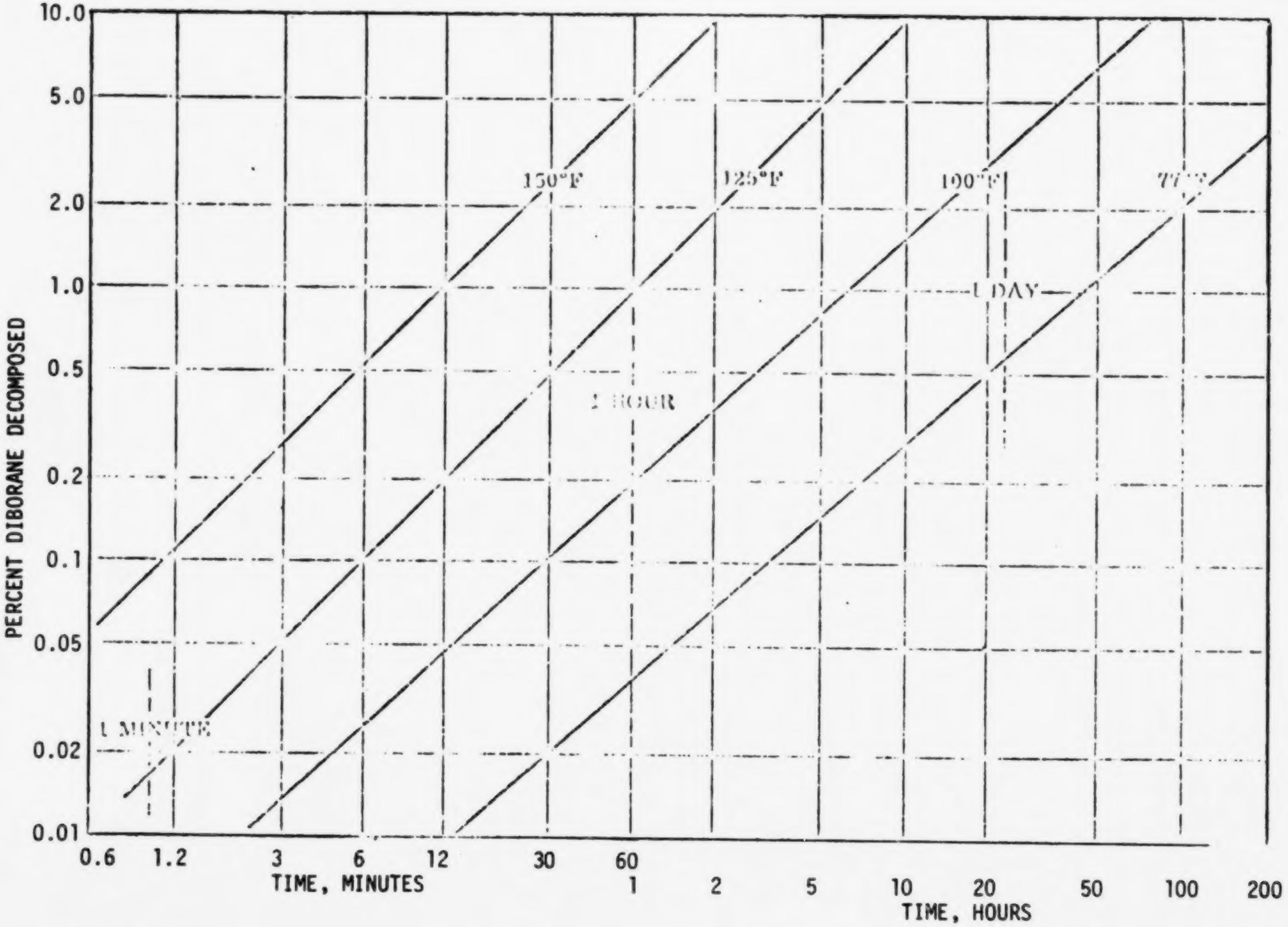


Figure 5.[1414] Diborance Decomposition

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation

Procedures for the handling, storage and transportation of boranes are well-documented.[2000,2092] Monitoring is complicated somewhat by the lack of convenient, specific detection apparatus, but since leakage is invariably accompanied by decomposition or polymerization with an accompanying evolution of hydrogen, the chemical and physical characteristics of a batch can be fairly easily determined by a search for hydrogen gas. The 200,000 lb of pentaboranes stored at Edwards Air Force Base, California is periodically inspected by civilian and military personnel for corrosion of the cylinder valves.[2007]

Only the three most stable boranes--diborane, pentaborane(9), and decaborance--are shipped in any quantity. It is preferred, but not required, that they be stored and shipped at cryogenic temperatures. In any case, space should be available for possible hydrogen evolution within the container. Department of Transportation Regulations[0278] makes no special material provisions for shipping containers, other than the general specifications for gases. Other specific requirements are:

Diborane	Special permit required.
Pentaborane (9)	Not acceptable for rail shipment.
Decaborane	25 lb maximum container.

Disposal and Reuse

Diborane: There is no generation of diborane or other hazardous waste in the production of diborane by the Callery Chemical Company. Waste is generated, however, when the 10 mole percent gas is diluted by Matheson, Air Products and Chemicals, or Linde, respectively. This waste is in the form of residual gas remaining in the manifolds after mixing is complete.

Air Products and Chemicals Inc. mixes diborane with H_2, N_2 or argon in three locations in the United States - Emmaus, Pennsylvania,[2017] Long Beach, California,[2015] and Houston, Texas. The Emmaus, Pennsylvania facility runs about 0.1 ft^3 every six months to a storage cylinder, which has been filling for six years and is currently half full. They are not concerned at present with disposal of this cylinder approximately six years hence. Used cylinders are returned to Callery, where they are probably burned. The Long Beach, California facility handles approximately 10 lb/yr of the 10 mole percent mixture. They occasionally vent "a few cc of the mixture" to the atmosphere with no monitoring or control. Used returned cylinders are burned with no control. The Houston facility operates similarly to the Long Beach facility.

The Linde Division of the Union Carbide Corporation mixes diborane in five locations - East Chicago, Indiana; Houston, Texas; Keaseby, New Jersey; Linden, New Jersey; and Torrance, California.[2018] The Torrance, California facility uses approximately 60 lb/yr of the 10 mole per cent mixture. After dilution there is usually a residual of 500 cc, which is disposed of either by:1) transferring it into a garbage cylinder and dumping the cylinder; 2) diluting with N_2 and venting to the atmosphere; 3) scrubbing with water and sewering; or 4) bubbling through 5 gal alcohol and venting the exhaust gases to the atmosphere in an uncontrolled manner. They claim never to have detected boron-containing compounds in the atmosphere.

Matheson Gas Products mixes diborane in three locations - Cucamonga, California,[2011] Newark, California,[2010] and East Rutherford, New Jersey. The East Rutherford facility burns all waste and vents the B_2O_3 particulate-laden waste to the atmosphere in an uncontrolled manner. The Cucamonga facility evacuates most of its waste into a garbage cylinder which is shipped to Newark for disposal. Some waste at Cucamonga is absorbed in aqueous ammonia. The resultant boric acid suspension is then sewered in compliance with local water district regulations, which specify a maximum 500 ppm suspended solids. The Newark facility absorbs all diborane waste in aqueous ammonia and meters it into the sewer system under regulations which specify a pH range of 6.4 to 7.8. No analysis is made of the effluent for the concentration of boron or boron-containing compounds.

Two typical semiconductor manufacturers were contacted--TRW Semiconductors, Lawndale, California,[2016] and Collins Radio Company, Newport Beach, California.[2012] In the TRW process, the B_2H_6 is completely reacted to B_2O_3 at 1100 C. Some is vented; the major portion, amounting to 0.2 g/mo, is sewered. In the Collins process, the exhaust gases containing B_2H_6 and B_2O_3 are scrubbed with water. The effluent is neutralized with NH_3, and returned to the sanitary water supply. A slight deposit has been accumulating over a period of time in the bottom of the neutralizing tank, which "is of no concern at present. It has never been chemically analyzed."[2012]

Pentaborane (9): The use of 50 to 75 lb/yr of pentaborane by Chemical Systems Inc., Santa Ana, California[2006] in the manufacture of their high temperature elastomer, Pentasil, generates no waste except H_2, which is vented. At Edwards Air Force Base, California[2007] periodic inspections of the 200,000 lb stockpile occasionally reveal a cylinder with a corroding valve, although none has been found in the past two years. Damaged cylinders are trucked to remote portions of the Mojave Desert, where they are exploded by machine gun fire.

Decaborane: The high value of decaborane causes the Olin Corporation[2008] to recycle all decaborane waste in the production of its high temperature elastomer, Dexsil. Consequently, there is no waste released to the environment. Its stockpile of decaborane is stored at cryogenic temperatures and is monitored for the evolution of hydrogen, which would signal decomposition.

The manufacture of decaborane by the Callery Chemical Company[2020] creates solid, toxic wastes, which are burned in an uncontrolled manner. No information is available on the ultimate disposition of decaborane used in classified research on solid propellants.

For the disposal of boranes, the acceptable criteria is defined in terms of the provisional limits for diborane, pentaborane, and decaborane:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Diborane	0.001 ppm (0.001 mg/M^3)	0.01 TLV
Pentaborane	0.00005 ppm (0.0001 mg/M^3)	0.01 TLV
Decaborane	0.0005 ppm (0.003 mg/M^3)	0.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Diborane	0.005 ppm (mg/l)	Stokinger and Woodward Method
Pentaborane	0.0005 ppm (mg/l)	Stokinger and Woodward Method
Decaborane	0.015 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Venting to the Atmosphere

This is the procedure used by many of the gas mixing plants for the disposal of residual diborane. Since the provisional limit for diborane in air is so stringent (0.001 ppm, corresponding to 1μg/m^3), it is doubtful if this limit is being met consistently. There is certainly no evidence for compliance. Attempts to obtain evidence are hindered by the lack of suitable detection equipment which is both portable and specific.[2092]

Option No.2 - Destruction by Burning or Explosion and Venting of Exhaust Products

This procedure is superior to simple venting, since the resultant particulate B_2O_3 is less hazardous than any of the boranes themselves. Here again, though, there is no evidence that the release of the B_2O_3 is being kept within safe limits. The gas-mixing plants which employ this procedure for the disposal of residual diborane and the Callery Chemical Company, which burns the toxic wastes resulting from the production of decaborane, are located in heavily populated areas, and the lack of information with regard to the B_2O_3 released is of concern. On the other hand, the disposal of occasional cylinders of pentaborane (9) by this method in isolated areas of the Mojave Desert is satisfactory. There is little concern for B_2O_3 leaching into any ground water, since the high-fired form is essentially insoluble.

Option No.3 - Wet Scrubbing and Sewering

The instability of boranes when in contact with water, particularly aqueous ammonia, is of great advantage, since hydrolysis occurs easily and goes quickly to completion. The outstanding concern, however, is the possible release of undesirable amounts of boric acid solution and low-fired B_2O_3 aqueous suspension to the environment.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Boranes have low Threshold Limit Values (TLV), are very difficult to detect, and appear in relatively small volumes. As such, they are ideal candidate waste stream constituents for National Disposal Sites. Also, there are no undue restrictions on shipment, so transport to National Disposal Sites will not prove difficult.

The current practices of venting boranes and their combustion and solution products (boric oxide and boric acid) must be regarded as unsatisfactory. No attempts are made to monitor air and water emissions. The relatively low volume of material and the technical difficulty of monitoring boron and its compounds would make routine analysis difficult and expensive for the gas mixing plants.

Since the waste diborane is already in a gastight system under high pressure, it would be relatively easy to evacuate it into a garbage cylinder for eventual shipment to a National Disposal Site. Similar procedures are already practiced by the Matheson Cucamonga plant when it ships its wastes to the Newark plant and by the Air Products Emmaus plant as it stores its waste indefinitely in its giant garbage cylinder. Similarly, the Callery Chemical Company would no doubt find it more convenient to ship its solid wastes from decaborane production to someone else, rather than burn them on its own property. Thus, the release of all boranes to the environment would essentially cease with possible benefit to all.

At the National Disposal Site, the recommended processes for borane disposal are:

Process	Order of Preference	Remarks
Incineration with aqueous scrubbing of exhaust gases to remove B_2O_3 particulates.	First Choice	Applicable to borane containing solid, liquid, and gaseous wastes.
Hydrolysis with subsequent evaporation to solid boric acid.	Second Choice	Generally not applicable to borane containing solid wastes.

For either processes, the borane wastes would be reduced to a low volume of relatively nonreactive, non-toxic solids.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Diborane (61)

Common Names Boron hydride, boroethane

Structural Formula

B_2H_6

Molecular Wt. 27.7 Melting Pt. -165.5 C Boiling Pt. -9.25 C

Density (Condensed) 0.577 @ -183 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

22 mm @ -112 C @ @

Flash Point -130 F Autoignition Temp. 100 -125 F

Flammability Limits in Air (wt %) Lower <0.9% Upper >98%

Explosive Limits in Air (wt. %) Lower 0.9% Upper 98%

Solubility

Cold Water dissociates Hot Water dissociates Ethanol

Others: NH_4OH

Acid, Base Properties slightly acidic

Highly Reactive with water or steam to produce H_2; reacts explosively with oxidizing materials; rubber, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel gas cylinders

ICC Classification flam-compressed gas, red label Coast Guard Classification

Comments Special Permit required.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ______

IUC Name Tetraborane (61)

Common Names Dihydrotetraborane, boron hydride, borobutane, tetraborondecahydride

Structural Formula

B_4H_{10}

Molecular Wt. 53.4   Melting Pt. -120 C   Boiling Pt. 18 C

Density (Condensed) 0.59 @ -70 C   Density (gas) 1.8 @ 6 C

Vapor Pressure (recommended 55 C and 20 C)

580 mm @ 6 C   ______ @ ______   ______ @ ______

Flash Point ______   Autoignition Temp. ______

Flammability Limits in Air (wt %)   Lower ______   Upper ______

Explosive Limits in Air (wt. %)   Lower ______   Upper ______

Solubility

Cold Water Hydrolyzes   Hot Water Hydrolyzes   Ethanol Dissociates

Others: Benzene

Acid, Base Properties slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with Stainless steel, most metals, asbestos, graphite

Shipped in not shipped

ICC Classification ______   Coast Guard Classification ______

Comments ______

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Pentaborane [9] (61, 505)

Structural Formula

B_5H_9

Common Names Pentaboron enneahydride, pentaborane (stable), boron hydride

Molecular Wt. 63.2 Melting Pt. -46.6 C Boiling Pt. 58.4 C

Density (Condensed) 0.61 @ 0 C Density (gas) 2.2 @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

66 mm @ 0 C @ @

Flash Point 30 C Autoignition Temp. 35 C

Flammability Limits in Air (wt %) Lower Spontaneously flam Upper

Explosive Limits in Air (wt. %) Lower 0.42% Upper

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol

Others:

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel gas cylinders

ICC Classification flam. liquid, red label Coast Guard Classification flam. liquid, red label

Comments Not acceptable by rail, Code of Federal regulations Sec. 73.138 MCA warning label

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Pentaborane [11] (61)

Common Names Dihydropentaborane, pentaborane (unstable), boron hydride

Structural Formula

B_5H_{11}

Molecular Wt. 65.2 Melting Pt. -123 C Boiling Pt. 63 C

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Spontaneously flam. Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol

Others:

Acid, Base Properties Slightly acidic.

Highly Reactive with Oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in Not shipped

ICC Classification flam. liquid, red label, not acceptable. Coast Guard Classification

Comments

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Hexaborane (61)

Common Names Boron hydride, hexaboron decahydride

Structural Formula

B_6H_{10}

Molecular Wt. 75.0

Melting Pt. -65.1 C

Boiling Pt. 0 C @ 7.2 mm

Density (Condensed) 0.69 @ 0 C

Density (gas) 2.6 @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

7.2 mm @ 0 C

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hydrolyzes

Hot Water Hydrolyzes

Ethanol

Others:

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in Not shipped

ICC Classification

Coast Guard Classification

Comments

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __________

IUC Name Decaborane (61)

Common Names Boron hydride, decaboron tetradecahydride

Structural Formula

$B_{10}H_{14}$

Molecular Wt. 122.3 Melting Pt. 99.7 C Boiling Pt. 213 C

Density (Condensed) 0.94 @ 20 C Density (gas) ______ @ ______ ______

Vapor Pressure (recommended 55 C and 20 C)

19 mm @ 100 C 66 mm @ 132 C ______ @ ______

Flash Point 80 C Autoignition Temp. 149 C

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water Slightly Hot Water Dissociates Ethanol Yes

Others: CS_2, ether, benzene

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel barrels or drums

ICC Classification flam.solid, yellow label,25lb Coast Guard Classification ______

Comments Code of Federal Regulations Sec. 73.236

PROFILE REPORT

Nitrocellulose (534)

1. GENERAL

Nitrocellulose (cellulose nitrate, or NC) is a mixture obtained by nitrating cellulose. Cellulose is a long chain polymer of anhydroglucose units. The hydrogen of the three hydroxyl units in each glucose unit in cellulose can be replaced by NO_2 groups. The nitrogen content of cellulose tri-nitrate is 14.14 percent. Although complete nitration is difficult to accomplish, materials containing 14 percent nitrogen can be prepared without difficulty. The nitration is carried out under conditions of acid concentration, temperature, and time of nitration which depend upon the final product desired.

For the manufacture of military grade nitrocellulose, the DuPont mechanical dipper technique is normally used. One advantage of the mechanical dipper process is that the cellulose can be quickly submerged in the mixed acid and the evolution of nitrogen oxides reduced. Between 30 and 40 lb of dry, fluffed cellulose (cotton linters or wood pulp) is the normal batch size added to the nitrating dipper containing a large excess (about 1,600 lb) of mixed acid (mixed sulfuric and nitric acids) at 30 C. The composition of the mixed acid is adjusted to the grade of nitrocellulose required. For gun cotton (13.3 percent N) the normal composition with wood pulp is 59.5 percent sulfuric, 28.5 percent nitric, 3.0 percent nitrosylsulfuric and 9.0 percent water. The nitration reaction is exothermic, and the charge temperature is kept below 34 C by cooling. After about 25 minutes in the nitrator, the charge is transferred rapidly to a centrifuge, the spent acid removed and then the nitrated cotton is drowned in a large excess of water. The spent acid is pumped to a tank where part of it is fortified for reuse and the remainder is sent to the acid recovery plant. The crude nitrocellulose is usually pumped as a water slurry to the purification area where it goes through an elaborate series of water washes, boiling treatments, neutralizations and beating

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steps to stabilize the nitrocellulose. First, the acid content is reduced to a low level by washing. Then, the nitrocellulose receives several boiling treatments to destroy the unstable sulfate esters and nitrates of partially oxidized cellulose by acid hydrolysis. The nitrocellulose is water washed between boils. Next, the product is beaten in a Jordan refiner to reduce the fiber length and remove traces of occluded acid. Finally, the nitrocellulose is boiled in dilute sodium carbonate solution, then washed with water until free of alkali. After purification, the NC is centrifuged for partial removal of water, and then processed in accordance with the specific end-use requirements of the batch. Nitrocellulose is used for military purposes in the manufacture of single base and double base propellants, as gun cotton, and commercially as collodion.[1142,1147]

Nitrocellulose fines recovered from the purification washing and centrifugation waste liquor sumps are generally destroyed by open burning. Some plants now recycle the recovered fines to production.

The physical/chemical properties of nitrocellulose are summarized in the attached worksheet.

2. TOXICOLOGY

Nitrocellulose presents no toxic hazard. However, when handling nitrocellulose wet with alcohol, the alcohol is usually denatured with 0.5 percent benzene which presents a benzene inhalation hazard.[1142]

3. OTHER HAZARDS

Dry nitrocellulose is very sensitive to impact, friction, heat and spark, and is an explosive hazard. Nitrocellulose wet with solvent is a dangerous fire hazard. Nitrocellulose wet with water is less dangerous. However, nitrocellulose can be detonated even when wet, if confined and initiated with a strong booster.[1142] Nitrocellulose has an impact sensitivity (2 Kg. wt) for a 5 Mg sample of 8 cm., roughly equivalent to the sensitivity of DDNP-a sensitive initiator.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Wash waters containing nitrocellulose particles and other scrap created during manufacturing operations are collected in sumps. After settling, nitrocellulose is collected, placed in drums under water and transported to the disposal area.[1142] Scrap propellant containing nitrocellulose, if free of aluminum powder, is also placed in drums under water and transported to the disposal area. If aluminum powder is present, the propellant containing nitrocellulose is stored dry because the aluminum reacts with water to produce hydrogen.

Dry nitrocellulose is classified by the Department of Transportation (DOT) as an Explosive, Class A. The weight limit per container is 10 lb of dry uncompressed nitrocellulose. Wet nitrocellulose (colloided, granular, or flake) with 20 percent water is classed as a flammable solid. Wet nitrocellulose (colloided, granular or flake) with 20 percent alcohol or solvent is classed by DOT as a flammable liquid. The alcohol is usually denatured ethanol, isopropanol or normal butanol. At no time is the alcohol entirely uniform throughout the drum. On standing, the alcohol gradually settles leaving the nitrocellulose on top with a lower alcohol content. Nitrocellulose undergoes very slow decomposition even at ordinary temperatures. Because of deterioration, nitrocellulose should be used within a few months after manufacture. Frequent stability checks (KI tests) should be made if the NC has been stored over one year.[1142]

Because of its sensitivity, no nitrocellulose should be released to the environment in waste streams.

The waste forms containing nitrocellulose are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert materials are almost always combustible wastes--cardboard, paperboard, fiberboard, and the like). The quantities by location of the nitrocellulose and of the waste forms in which it is contained are included in the quantities listed under the headings "Propellant, Nitrocellulose Based" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV titled Waste Forms and Quantities.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of nitrocellulose are briefly described in the following paragraphs together with recommendations as to adequacy.

Option No. 1 - Disposal of Burning

Nitrocellulose for destruction is usually placed in fiberboard drums, metal drums or cans lined with a heavy-gauge leakproof liner and the nitrocellulose covered with water. The nitrocellulose is then transported to an approved burning ground. The NC wastes are placed on a noncombustible pad such as asbestos, the water allowed to drain off, and the NC wastes are then covered with a combustible material such as fuel oil. The flammable material is ignited by firing a black powder squib or other device placed in the wastes.[1142] Although the products of combustion contain considerable NO_x, better methods for disposal are not currently in wide use.

Option No. 2 - Controlled Incineration

Nitrocellulose wastes, and combustible materials contaminated with nitrocellulose are readily amenable to disposal via controlled incineration. Two types of equipment are currently in prototype use for the controlled combustion of explosive wastes. The first disposal system is similar to conveyor fed devices used as muncipal incinerators, operates on an induced draft, and is equipped with afterburner and scrubbing systems to abate NO_x and particulate emissions. The second type of equipment, similarly equipped with scrubbing systems for the abatement of NO_x and particulate emissions, is a rotary kiln incinerator, which is fed with a slurry of nitrocellulose in water, in a 1 to 3 ratio. The rotary kiln incinerator has secondary fuel oil or natural gas burners. This method of disposal is preferred.

Option No. 3 - Reduction with Sodium Hydroxide

Small quantities of nitrocellulose are decomposed by adding it with agitation to five times its weight of a 10 percent solution of sodium hydroxide that has been heated to 70 C. Agitation is continued for at least 15 minutes after all the nitrocellulose has been added.[1147] The products of this decomposition process require additional treatment. After pH adjustment and dilution, the cellulose can be handled by a sewage treatment plant.

Option No. 4 - Controlled Incineration of Obsolete Munitions

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of small charges of high explosive (such as nitrocellulose). High explosives up to about 7 lb in weight per charge, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major uses of nitrocellulose are in the manufacture of single and double base propellants and smokeless powder. The open burning which is widely used is not considered satisfactory for destroying the large quantities (millions of pounds) of excess or waste material containing nitrocellulose. Wastes other than obsolete munitions containing nitrocellulose which is excess, contaminated or aged are candidates for disposal at National Disposal Sites if the specific wastes can be handled safely and transported safely. The methods for controlled incineration that were discussed in Section 5, Option No. 4 should be used for destroying non-defense excess material or wastes containing nitrocellulose at National Disposal Sites. Nitrocellulose for disposal should be transported under water, in a vehicle properly equipped for safe transport of flammable liquids to the nearest satisfactory disposal site. Surplus, scrap or obsolete material containing nitrocellulose should only be handled by qualified ordnance demolition personnel experienced in the disposal of explosives. If hazards to the disposal team and the public, due to handling and transportation to the nearest National Disposal Site are deemed excessive by the demolition team, the material should be disposed of by burning in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of nitrocellulose contained in obsolete military ordnance devices should be that of Option No. 3 above.

7. REFERENCES

1142. JANAF Hazards Working Group. Chemical rocket propellant hazards. V 2. CPIA Publication No. 194, Silver Springs, Maryland. May 1970. 99 p.

1147. Department of the Army and Air Force. Military explosives, TM-1910. Washington, Apr. 1955. 336 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitrocellulose (534)

IUC Name Cellulose Nitrate

Common Names NC

Structural Formula

$[C_6H_{10}O_5(NO_2)_x]_n$
x = no of NO_2 groups
n = degree of polymerizatio

Molecular Wt. 272.3(one unit)(1) Melting Pt. 200 C in vac(1) Boiling Pt. decomposes(1)

Density (Condensed) 1.66 g/cc @ 23 C Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water Insoluble(1) Hot Water Insoluble(1) Ethanol Insoluble

Others: Soluble acetone, organic nitro compounds(1)

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Shipped in Waterproof containers

ICC Classification Explosive, Class A(dry)(1) Coast Guard Classification Explosive Class A(dry)(1)

Comments ____

References (1) 1142

PROFILE REPORT

Gelatinized Nitrocellulose(PNC)(523)

1. GENERAL

Gelatinized nitrocellulose, which is often called plastisol nitrocellulose (PNC), is a white powder made up of spherical particles or aggregates of spherical particles. PNC does not have a definite chemical composition but varies from $C_{12}H_{17}(ONO_2)_3O_7$ to $C_{12}H_{14}(ONO_2)_6O_4$. Different impurities will be present which depend on the location of manufacture. PNC is used in the manufacture of solid propellant.[1142] The physical/chemical properties of PNC are summarized in the attached worksheet.

2. TOXICOLOGY

PNC is not generally considered toxic as such, or reactive with the skin. In a wet condition, however, the solvents used in its manufacture or for shipping may be dangerous and present the greatest toxicity hazard in its handling. For example, PNC made at the Naval Ordnance Station contains nitromethane because of its method of manufacture.[1142]

3. OTHER HAZARDS

Dry PNC is an extreme fire hazard, and proper care should be taken in its handling and storage. It should be handled or transported in conductive containers, which should be grounded at all times. Stainless steel is recommended for this service, since PNC may be affected by some metals. For storage and handling it should be treated the same as nitrocellulose, and, in general the explosive hazard should be considered similar to that of nitrocellulose.[1142] The precautions noted in the Profile Report on Nitrocellulose (534) should be adopted in handling PNC. Although PNC is not listed by the Department of Transportation (DOT), the dry material should probably be classified as Explosive, Class A.

PNC is less dangerous when stored wet with solvents or water. Due to the flammability of many of the solvents, a fire hazard still exists.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of PNC to fire and explosion, as with nitrocellulose, requires that all scrap and waste from preparation be maintained wet for destruction. Waste PNC should be collected in drums or fiberboard containers lined with conductive polyethylene bags.

Because PNC is an explosive and fire hazard, it is recommended that no PNC be released to the environment. The waste forms containing PNC are for the most part surplus obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes- cardboard, paperboard, fiberboard, and the like). The quantities by location of the PNC and of the waste forms in which it is contained, are included in the quantities listed under the headings "Propellant, Nitrocelluose Base" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV of this report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Open Burning

The only process widely used for disposal of surplus, scrap or obsolete PNC is burning. The methods used for burning are generally in compliance with the procedures outlined in the military safety manuals.[2170,2230] PNC waste is placed in steel drums or fiberboard drums lined with conductive polyethylene bags. The PNC is covered with water, the drum closed and transported to a burning ground. The bags are removed, placed on straw or other flammable material, and the PNC and straw ignited with a black powder squib.[1142] As with all compounds containing nitro groups, considerable NO_x is released upon burning. This technique is therefore unsatisfactory.

Option No. 2 - Controlled Incineration

PNC wastes are readily amenable to controlled incineration. The two types of equipment in prototype use currently for this service are both afterburner and scrubber equipped, produce gaseous effluents stripped of NO_x and are equally acceptable from an environmental standpoint. The first disposal system is a municipal incinerator, fed by a conveyor, and possesses some minor safety drawbacks. The second type of equipment is a rotary kiln incinerator, which is fed with a slurry of explosive in water, in a 1 to 3 ratio. This method of disposal is preferred.

Option No. 3 - The Chemical Agent Munition Disposal System

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a Deactivation Furnace which is particularly suited to the disposal of small charges of high explosive (such as PNC). High explosives up to about 7 lb in weight per charge, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

PNC is manufactured and used at propellant manufacturing plants that have facilities for the disposal of surplus, scrap or obsolete PNC or propellant containing PNC. Disposal of PNC at these facilities by open burning is unsatisfactory. PNC wastes other than military munitions which are not destroyed by controlled incineration, as per Option No. 2 above, are candidates for National Disposal Sites. The disposal process recommended is that of Option No. 2. The wastes should be handled and transported only by a qualified ordnance disposal team. PNC wastes should be transported wet, in containers as noted in Section 4, to the nearest National Disposal Site.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of PNC after disassembly of the military ordnance devices, should be that of Option No. 3.

7. REFERENCES

1142. JANAF Hazards Working Group. Chemical rocket propellant hazards. v.2. CPIA Publication.

2170. Ordnance Corp, Department of the Army. Ordnance safety manual, ORDM7-224, Washington. 1951.

2230. Department of the Air Force. Explosive safety manual, AF Manual AFM127-100. Washington. Dec. 2, 1971.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Gelatinized nitrocellulose (523)

IUC Name

Common Names Plastisol Nitrocellulose(PNC)

Structural Formula

$C_{12}H_{17}(ONO_2)_3O_7$ to
$C_{12}H_{14}(ONO_2)_6)_4$

Molecular Wt. 459.28 to 594.29(1) Melting Pt. none Boiling Pt.

Density (Condensed) 1.55g/cc @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp. 160 C(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Insoluble Ethanol Insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Stainless steel drums

ICC Classification None Coast Guard Classification None

Comments

References (1) 1142

PROFILE REPORT

Perchloryl Fluoride (326)

1. GENERAL

Perchloryl fluoride, ClO_3F, is the acyl fluoride of perchloric acid. It is a stable compound of low reactivity that is shipped as a compressed gas. Perchloryl fluoride gas is colorless and the liquid is clean and water-white. It has a characteristic sweet odor. The oxidizing potential of perchloryl fluoride is high which has resulted in its evaluation as a storable liquid oxidizer for rockets. In an alkaline environment, perchloryl fluoride selectively replaces labile hydrogen with fluorine; this property is in use in the preparation of certain fluoro-steroids. In the presence of Friedel-Crafts catalysts, perchloryl fluoride can introduce the ClO_3 ground onto aromatic rings giving a new class of perchloryl aromatic compounds.

Perchloryl fluoride is prepared by the electroysis of sodium perchlorate dissolved in anhydrous hydrogen fluoride. The stability of perchloryl fluoride is due to its molecular symmetry. On the other hand, its component elements can be released at a controlled rate. Anhydrous perchloryl fluforide is thermally stable up to 500 C. The chemical reactivity is primarily dependent on pH, temperature and the presence of the other reactive atoms or molecules in the reaction media. It is resistant to hydrolysis; water at 250 to 300 C has very little effect on perchloryl fluroide. In sealed tubes at 250 to 300 C it reacts with alkali metal hydroxides to give a quantitative hydrolysis to perchlorate and fluoride ions. Alcoholic potassium hydroxide causes rapid hydrolysis of perchloryl fluoride at 25 C. [2152]

The physical/chemical properties for perchloryl fluoride are given in the attached worksheet.

2. TOXICOLOGY

Should liquid perchloryl fluoride splash on the skin, moderate to severe frostbite "burns" may occur depending on the amount spilled and the length of time on the skin. However, toxic injury to the skin is unlikely.

Moderate to high concentration of the vapor causes respiratory irritation and methemoglobinemia. If severe, methemoglobinemia is accompanied by cyanosis. Repeated long term exposure to low concentrations of perchloryl fluoride may cause fluorosis of fluoride deposition in bones and teeth. This conclusion is based on the detection of significant increases of fluoride concentrations in the blood, urine and bones of rats, dogs, and guinea pigs exposed to 25 ppm concentrations for six months.[2153]

The Threshold Limit Value (TLV) for an 8-hour day, 5 days per week is 13.5 mg/m^3 (3 ppm) (ACGIH).[0225] The maximum emergency exposure limits are as follows:[1300]

10 minutes	170 mg/m^3	(50 ppm)
30 minutes	68 mg/m^3	(20 ppm)
60 minutes	34 mg/m^3	(10 ppm)

3. OTHER HAZARDS

A system containing liquified perchloryl fluoride in the presence of an oxidizable substance may be shock sensitive, in a fashion similar to that encountered with liquid oxygen. Therefore, caution must be exercised to prevent contamination of perchloryl fluoride from occurring. No attempt should be made to absorb, condense, or liquify effluent gases from reactions.[1300,2154]

Many perchloryl derivatives, both organic and inorganic, demonstrate shock sensitivity. Sufficient heat or mechanical impact may cause detonation.[2154]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Anhydrous perchloryl fluoride does not attack glass, corrode metals, or attack common gasketing materials rapidly at ordinary temperatures. It can be stored for extended periods, as shipped, ready for immediate use. Anhydrous perchloryl fluoride has been stored at 70 F in steel cylinders for periods of several years without evidence of instability. Shorter term storage tests at 100 F have given equally favorable results.[2153]

The maximum temperature recommended for prolonged storage in metal containers is 130 F. Perchloryl fluoride in gaseous and liquid states is stable to shock.[2154]

In the presence of water vapor, perchloryl fluoride becomes corrosive to many metals. Stainless steels, types 304, 310 and 314 have shown favorable short-term exposure tests at 25 C for two-month exposure. Other metals exhibiting good resistance under these conditions include Hastelloy, titanium and tantalum.[2154]

Perchloryl fluoride is shipped by rail or truck. Air freight, parcel post, and rail express are permitted; it is not approved for air express shipment. The loaded pressure in cylinders at 70 F is 145 psig. Perchloryl fluoride is classified by the U. S. Department of Transportation (DOT) as a "Compressed Gas, Not Otherwise Specified." A green DOT label is required during shipment.[2153]

The safe disposal of perchloryl fluoride is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Perchloryl Fluoride	0.025 mg/M3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Perchloryl Fluoride	0.61 to 1.7 ppm	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of perchloryl fluoride are briefly described in the following paragraphs together with recommendations as to their adequacy. Detailed discussions of the processing operations are presented in the referenced perchloryl fluoride reports.

Option No. 1 - Reaction with a Charcoal Bed

The classic fluorine disposal unit is a charcoal bed composed of 3/8-in. charcoal bits.[1154] This method has been used with fluorine, with interhalogen compounds (ClF_3 and ClF_5) and with perchloryl fluoride.[1300] The products are carbon tetrafluoride, carbon dioxide, and chlorine. Carbon tetrafluoride is chemically inert and relatively non-toxic which permits it to be vented.[1414] Chlorine and carbon dioxide produced are removed by a caustic scrubber. Perchloryl fluoride is highly hypergolic with either amorphous carbon or charcoal and reacts vigorously under all conditions, even at low concentrations.[2154] If high rates of disposal are required for perchloryl fluoride, the charcoal reactor will become a huge furnace. However, for fluorine, the charcoal disposal system has proven successful for disposal rates up to 600 lb per hr (30 lb of fluorine in approximately 3 min). Continuous operation requires a number of parallel disposal reactors. Approximately 17 lb of charcoal are required to treat 100 lb of fluorine.[1154,1414] On this basis, about 22 lb of charcoal would be required per 100 lb of ClO_3F. Engineering data for perchloryl fluoride similar to that obtained for fluorine has not been obtained, but is required to adequately design a charcoal reactor for perchloryl fluoride.

Option No. 2 - Propane Burner

A propane burner has been described for the disposal of oxygen difluoride which could be used for perchloryl fluoride.[1414] The unit consists of a burner, stack, propane supply and control system and an air blower. The fluorine compound is discharged into the burner, which is run rich in propane. Both hydrogen fluoride and chloride are exhausted and require scrubbing. Such a unit, though not in use, should be satisfactory for treating large quantities of perchloryl fluoride.

Option No. 3 - Venting

One propellant handling manual recommends disposal of perchloryl fluoride in an isolated, posted area by remotely controlled dumping through a pipe to a shallow evaporating pan where the material is allowed to evaporate.[1300] This method is not considered satisfactory because the vapors discharged are reactive and toxic.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is recommended that National Disposal Sites have a unit operation capable of handling perchloryl fluoride, fluorine, interhalogen compounds and chlorine. Since this unit operation will not be required to handle large volumes of these compounds, the unit can contain options for treating each of these compounds. It is recommended that experimentation be conducted to generate the necessary engineering data for construction of such a unit. Option 1, Reaction with a Charcoal Bed, is recommended for use at a National Disposal Site because this method has been adequately evaluated for treatment of fluorine and has been used in the laboratory for treatment of perchloryl fluoride.

7. REFERENCES

0225. American Conference of Governmental Industrial Hygienists. Threshold limit values for 1971. Occupational Hazards, p. 35-40, Aug. 1971.

1154. Cakle, F. S. Design handbook for liquid fluorine, general handling equipment, WADD Technical Report 60-159, AGC Contract AF 36(616)6586, Dec. 1960.

1300. Joint Army Navy AirForce (JANAF) Hazards Working Group. Chemical rocket propellant hazards, liquid propellant handling, storage and transportation, VIII, CPIA Publication No.194, May 1970, Silver Springs, Maryland.

1414. Convair Division of General Dynamics. A study of prelaunch operations for a space storable propellant module. Final Report No. GDC-BNZ 69-013-7, San Diego, California.

2152. Personal communication. Dr. John F. Gall, Pennsalt Chemicals Corporation, to J. R. Denson, TRW Systems, Feb. 1966.

2153. Pennsalt Chemicals Corporation. Perchloryl fluoride, New Products Booklet DS-1819, Philadelphia. 6 p.

2154. Pennsalt Chemical Corporation. Perchloryl fluoride. New Products Booklet DS-1819, Philadelphia. 24 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Perchloryl fluoride (326)

IUC Name Perchloryl fluoride

Common Names

Structural Formula

ClO_3F

Molecular Wt. 102.45 Melting Pt. -147.7 C Boiling Pt. -46.67 C

Density (Condensed) 2.003 @147.7 C Density (gas) 0.065 g/cm^2 @ 25 C

Vapor Pressure (recommended 55 C and 20 C)

2.25 psia @ -80 C 84.01 psia @ 0 C 176.0 psia @ 25 C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.1 g/l at 25 C Hot Water Ethanol 2.5 g/l at 25 C

Others: dioxane 5.0 g/l at 25 C

Acid, Base Properties acts as a Lewis base in Friedel-Crafts type reactions

Highly Reactive with H_2S, N_2H_4, nucleophilic groups, carbon

Compatible with most metals, water

Shipped in steel cylinders

ICC Classification compressed gas, nos Coast Guard Classification compressed gas nos

Comments critical temperature 95.9 C
critical pressure 779 psia

References (1) 2154

PROFILE REPORT

Ammonium Picrate, Dry (27), Ammonium Picrate, Wet (28)

1. GENERAL

Ammonium picrate, ammonium 2,4,6-trinitrophenate, or Explosive D, is a colored crystalline compound. It exists in two forms; stable yellow monoclinic crystals and metastable red rhombic crystals. The two forms are easily interconvertible and do not differ in explosive properties. It is used as an explosive in armor-piercing projectiles and as an ingredient of picratol and propellant compositions. Ammonium picrate is less sensitive to impact than TNT, but has a lower temperature for explosion (318 C) than that for TNT (475 C). There are two classes of ammonium picrate for military use, which differ in particle size. Wet ammonium picrate is not used as an explosive but may be used as a convenient form for transportation.

The manufacture of ammonium picrate is accomplished by suspending picric acid in hot water and neutralizing the acid with gaseous aqueous ammonia. As the ammonia picrate forms, it goes into solution. Upon cooling the neutral solution, ammonium picrate separates as crystals which are washed with cold water. Chemically ammonium picrate is not very reactive. Strong alkalies decompose it into picric acid and ammonia. When maintained at its melting point, it decomposes into the same products.[0474,1147]

The chemical/physical properties for the ammonium picrates are summarized on the attached worksheet.

2. TOXICOLOGY

Ammonium picrate is not markedly toxic, but it discolors the skin and may cause a dermatitis. Inhalation of the dust should be avoided, and frequent baths and changes of clothing are prescribed for workers in production and use of ammonium picrate. Neither Threshold Limit Values (TLV), nor provisional maximum concentrations in water for man or fish, have been established. However, it can be assumed that the TLV of 0.1 mg per cubic meter for picric acid will also apply to ammonium picrate.

3. OTHER HAZARDS

Ammonium picrate is a high explosive that normally requires a primer train (initiating agent and booster) for detonation, although it may detonate when subjected to a flame. It is not as sensitive to shock as TNT.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The explosive characteristics of ammonium picrate require that all waste streams from its manufacture and all scrap conventional munitions containing ammonium picrate be treated by one of the disposal processes described as "acceptable" in Section 5, where recovery and reuse of the explosive is not economically feasible. Ammonium picrate, dry, is classed by the Department of Transportation (DOT) as an Explosive, Class A. In quantities less than 16 oz, wet ammonium picrate (minimum 10 percent water) may be shipped as an Inflammable Solid.

The safe disposal of ammonium picrate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These are:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Ammonium Picrate	0.001 mg/M^3 as Picric Acid	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Ammonium Picrate	0.005 mg/l as Picric Acid	Stokinger and Woodward Method

The majority of wastes containing ammonium picrate are discharged as manufacturing wastes, or are present as explosive Fill in, scrap conventional munitions. The quantities of these waste forms are included in those listed in Volume XIV.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No.1 - Chemical Degradation

Ammonium picrate in aqueous waste streams or excess ammonium picrate is decomposed by reaction with a considerable excess of sodium sulfide solution. The proportions employed are, by weight, one part explosive to 30 parts of 14 percent (by weight) hydrated sodium sulfide solution.[0474, 1147] The H_2S and NH_3 liberated must be scrubbed from the vent air, or burned in an appropriate scrubber-equipped incinerator. The solution from the disposal process must be neutralized, stripped of H_2S, and chlorinated to oxidize the remaining phenolics. The H_2S stripped from the solution should be burned in an appropriate, scrubber equipped incinerator. As an alternative to chlorination, the phenolics may be removed by adsorption on activated carbon. This technique is acceptable and is employed where the quantities of explosive treated are small or where explosive contaminated equipment must be decontaminated.

Option No.2 - Controlled Incineration - Manufacturing Wastes

The Army Ammunition Plants are currently investigating controlled incineration processes for the disposal of waste high explosives and high explosive-contaminated wastes. The systems under investigation include a conveyor-fed municipal type incinerator equipped with an afterburner, cyclones and wet scrubbers and a slurry-fed rotary kiln incinerator equipped with particulate abatement and wet scrubbing devices. Disposal systems of these types, when developed, are expected to be acceptable for use where recovery is not feasible economically, or where contaminated inert wastes must be destroyed.

Option No. 3 - Controlled Incineration - Military Munitions

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a Deactivation Furnace which is particularly suited to the disposal of small charges of high explosive (such as ammonium picrate). High explosives up to about 7 lb in weight per charge, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

Option No. 4 - Open Burning

The current procedure employed for disposal of the majority of the ammonium picrate manufacturing wastes is open burning in a safe area. This practice is unacceptable.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The ammonium picrate and picrate-contaminated inert wastes produced as manufacturing wastes should be disposed of at the plant site by Options 1, 2 or 3 of Section 5 above, in accordance with the quantity and character of explosive scrap involved. Conventional munitions classified as surplus which contain ammonium picrate explosive fill should be disposed of by the Armed Services at National Disposal Sites under Armed Service cognizance, by the technique of Option 3, above.

7. REFERENCES

0225. American Conference of Government Industrial Hygienists. Threshold limit values for 1971. Occupational Hazards, p. 35-40, Aug. 1971.

0474. Tomlinson, W. R. Jr., revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Rev. 1, Picatinny Arsenal. Apr. 1958. 348 p.

1147. Department of the Army and the Air Force. Military explosives, TM-9-1910, Washington. Apr. 1958. 336 p.

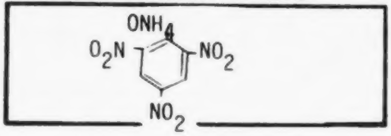
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ammonium Picrate (27)(28)

IUC Name Ammonium Picrate

Common Names

Structural Formula



Molecular Wt. 246.14 (1) Melting Pt. decomposes (1) Boiling Pt.

Density (Condensed) 1.72 (2) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp. 423 C explodes (1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1g/100g at 20 C (2) Hot Water Ethanol Slightly soluble (2)

Others:

Acid, Base Properties

Highly Reactive with strong base (2)

Compatible with

Shipped in

ICC Classification High Explosive (1) Coast Guard Classification High Explosive (1)

Comments

References (1) 0766
(2) 1492

PROFILE REPORT

Copper Acetylide (517) and Silver Acetylide (537)

1. GENERAL

The heavy metal salts of acetylene have the properties of primary explosives, but only cuprous acetylide has been found satisfactory for practical use. Cuprous acetylide is a russet or reddish-brown powder. It is prepared by the action of acetylene on an ammonia solution of cuprous chloride. In order to avoid contamination with cupric acetylide, a very sensitive explosive, cuprous acetylide is often precipitated in the presence of a reducing substance such as hydroxylamine, hydrazine sulfate, or sulfur dioxide. Cuprous acetylide forms as an impurity in hydrocarbon gas streams contaminated with acetylene when pipes or containers are contaminated with copper or copper-containing compounds. Cuprous acetylide explodes in air at 120 to 123 C, but in an acetylene atmosphere, under a pressure of 5 atm, it decomposes without explosion at 250 C. Cuprous acetylide is used as the chief component of match heads in electric fuses, being particularly susceptible to ignition by sparks or a glowing wire to give a sharp, hot flame.[2171] The physical/chemical properties of cuprous acetylide are summarized in the attached worksheet.

Silver acetylide, Ag_2C_2, is a white powder formed when acetylene is passed through an ammonical solution of silver chloride. It has even stronger explosive properties than cuprous acetylide due to its large negative heat of formation, $-\Delta H = 87.15$ Kcal/mole. It is of no practical use and has not been thoroughly characterized.[2171] It is not discussed further in this Profile Report.

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2. TOXICOLOGY

Although the toxicity of cuprous acetylide has not been well established,[0766] it is considered to be less toxic than other copper compounds, due to its low solubility in body fluids.

3. OTHER HAZARDS

Cuprous acetylide is a primary, initiating explosive so sensitive to heat, sparks, impact and friction that it undergoes detonation when subjected to very mild thermal, electrical or mechanical shock by a spark, flame or percussion. Care must be taken that cuprous acetylide is not contaminated with cupric acetylide which may occur if cuprous chloride used in the preparation of the acetylide contains cupric salt. This is important since cupric acetylide is unstable and explodes on heating even between 50 and 70 C, and is even more sensitive to impact and friction than cuprous acetylide.[2171]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of cuprous acetylide to shock, friction, and heat as with most initiating agents, requires that all scrap and waste from preparation and purification be maintained wet for destruction. Cuprous acetylide is packaged wet for storage or shipment. Packaging is accomplished by placing not more than 25 lb, wet with 20 percent water, in a duck-cloth or rubberized-cloth bag covered with a cap of the same material. The bag is then tied securely. Not more than six such bags are placed in the center of a watertight metal or wooden barrel, drum, or keg lined with a heavy close-fitting jute bag. The large bag containing cuprous acetylide is surrounded with well packed sawdust that has been saturated with water. The bag forming a liner is sewn closed before closing the barrel, drum, or keg. Not more than 150 lb of initiating explosive is permitted in a single container. It is shipped wet under the Department of Transportation (DOT) regulations for an Explosive, Class A.[2170]

Because cuprous acetylide is a sensitive primary explosive, it is recommended that no cuprous acetylide be released to the environment.

The safe disposal of cuprous acetylide is defined in terms of the recommended provisional limits for copper as a product of disposal in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Copper (in dust and mists)	0.01 mg/M^3 as Cu	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Copper	1.0 mg/l as Cu	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The only documented disposal process for cuprous acetylide is by detonation which is the disposal process generally employed for initiating explosives. Wet bags in the transporting container (described in Section 4) are transported to the disposal area. Then several bags are removed from the transporting container, carried to the destruction pit, placed in intimate contact with each other, and blasting caps are placed between the bags to initiate the cuprous acetylide. Remaining explosives must be kept behind a barricade with overhead protection during the destruction operations and located at a distance that assures safety. Personnel must be behind a similar barricade.[2170]

This disposal process is satisfactory on an interim basis, providing that copper salts liberated are not allowed to leach into ground water or near-by streams. Research is required to establish a fully satisfactory process for disposal of cuprous acetylide.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Cuprous acetylide is manufactured in limited quantities at plants making special electric fuses. Plants manufacturing such items have facilities for the disposal of cuprous acetylide discharged in waste streams, as scrap, or as excess material. Cuprous acetylide which is not processed for disposal at such manufacturers' facilities is a candidate waste stream constituent for National Disposal Sites if the specific waste involved can be handled and transported safely. This disposal process to be employed at National Disposal Sites should be the open detonation procedure accepted as satisfactory on an interim basis in Section 5, until a fully satisfactory technique is developed. Surplus, scrap or obsolete materials containing copper acetylide should be handled only by qualified ordnance demolition personnel experienced in disposal of high sensitivity initiating explosives. The contaminated or scrap acetylide should be transported wet, in a vehicle properly equipped for safe transport of initiating explosives, and only to the nearest satisfactory disposal site. In the event that hazards to the disposal team and the public due to handling and transport to the nearest National Disposal Site are deemed excessive by the demolition team, the materials should be disposed of by detonation in a cleared area.

7. REFERENCES

0766. Sax, N. I., Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corporation. 1968. 251 p.

2170. Ordnance Corps, Department of the Army. Ordnance safety manual. ORDM-224, Washington. 1951.

2171. Urbanski, Todeusz, Chemistry and technology of explosives, V.III, Warsawa, Polish Scientific Publishers, 1967. Translated by Jurecki, Marian, New York, Pergamon Press. 714 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Cuprous acetylide

Common Names

Structural Formula

Cu_2C_2

Molecular Wt. 150.1(1)
Melting Pt. 120 C explodes
Boiling Pt.

Density (Condensed) @
Density (gas) @

Vapor Pressure (recommended 55°C and 20°C)

@ @ @

Flash Point
Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper
Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble
Hot Water Insoluble
Ethanol Insoluble
Others: Most organic solvents - insoluble, soluble in alkalies, KCN

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, wet

ICC Classification Explosive, Class A
Coast Guard Classification Explosive, Class A

Comments

References (1) 0766

PROFILE REPORT

Copper Chlorotetrazole (518), Gold Fulminate (fulminating gold) (526), Silver Styphnate (539), Silver Tetrazene (540)

1. GENERAL

The compounds copper chlorotetrazole, gold fulminate, silver styphnate and silver tetranzene are described in the unclassified literature only to the extent that they can be prepared.[2171,0474] Copper chlorotetrazole is classified as a sensitive primary explosive.[0474] Other fulminates, styphnates, and tetrazene salts are vigorous primary explosives capable of being used as initiators, and it is therefore assumed that gold fulminate, silver styphnate, and silver tetrazene will have similar properties. The worksheets summarizing physical/chemical properties and the details of toxicology are not presented for these compounds because this data is not available.

2. TOXICOLOGY

It should be noted that copper, gold and silver compounds are in general, only slightly toxic, and that isocyanates and styphnates have variable toxicity. No other data is available on the specific toxicology of the subject compounds.

3. OTHER HAZARDS

The four compounds discussed in this Profile Report are believed to be so sensitive to heat, impact, electrical discharge, and friction that they undergo detonation when subjected to a very mild thermal, mechanical, or electrical shock by a spark, flame, or percussion.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

If the four compounds discussed are manufactured, waste from precipitation and washing operations should be collected in settling tanks for treatment by the processes described in Section 5. Excess material should also be disposed of in the same manner. All waste should be kept wet until treated.

Though these compounds are not classified by the Department of Transportation (DOT) it appears they would be classified as an Explosive, Class A, and would be classified by the Army as Class 9, Group M explosives.[2170,0474]

The safe disposal of copper chlorotetrazole, silver styphnate and silver tetrazene is defined in terms of the recommended provisional limits for the copper and silver in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Copper (in dusts & mists)	0.01 mg/M^3 as Cu	0.01 TLV
Silver	0.0001 mg/M^3 as Ag	0.01 TLV
Contaminant in Water and Soil	**Provisional Limit**	**Basis for Recommendation**
Copper	1.0 mg/l as Cu	Drinking Water Standard
Silver	0.05 mg/l as Ag	Drinking Water Standard

Provisional limits have as yet not been established for gold compounds.

The four initiating agents covered in this Profile Report do not occur in any known waste stream, and are not currently used in U.S. manufactured munitions. If they have been discharged as waste, the quantities involved have been experimental lot quantities, probably less than 10 lb in the aggregate.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

These four compounds are not manufactured at present, and specific disposal procedures have not been published. With some modifications, the procedures used for the disposal of other detonating agents can be employed.

Option No. 1 - Detonation

The Ordnance Safety Manual recommends detonation as the best method for disposal of all initiating explosives.[2170] In the use of this procedure, bags containing the wet explosive are transported to the demolition area. Several bags are removed from the container and carried to the destruction pit, placed in intimate contact with each other, and a blasting cap placed between the bags to initiate the explosives. All remaining explosives should be kept behind a barricade with overhead protection during destruction operations. In the use of this method, the copper, gold, or silver present cannot be recovered, but will be lost to the soil in the demolition area. This method is not environmentally acceptable and should not be used unless the hazards of transportation and handling for disposal via the technique of Option No. 2 outweigh the ecological impact of detonation.

Option No. 2 - Controlled Combustion

The most promising technique under development for disposal of high explosives is the controlled combustion process which employs a rotary kiln incinerator equipped with appropriate scrubbing devices. This technique can probably be used with these four compounds. The explosive is fed to the incinerator as a slurry in water, at a weight ratio, explosive to water, of 1:3. The scrubber effluent would require treatment for recovery of particulate copper, gold or silver compounds formed as a combustion product. Additional copper, gold or silver could be recovered from the incinerator. This process is recommended for disposal of the four compounds being discussed.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The four compounds discussed, if used, would be used as initiating agents in military ammunition. Military ammunition manufacturing plants and ammunition storage depots have facilities for disposal of explosives discharged as scrap, or as contaminants of other wastes. Explosives which are not processed for disposal at such facilities are candidates for National Disposal Sites if the specific waste can be handled and transported safely. The explosives should be transported wet in a vehicle specially equipped for the safe transport of primary explosives, and only to the nearest disposal site. The disposal process to be employed at National Disposal Sites should be that cited as Option No. 2 in Section 5. Wastes of the compounds, and wastes contaminated with the compounds should be handled only by a qualified ordnance demolition team experienced in handling primary explosives. If hazards to the team and public from transportation and handling are deemed excessive by the demolition team, the waste should be disposed of by detonation in a cleared area.

7. REFERENCES

2170. Ordnance Corps., Department of the Army. Ordnance safety manual, ORDM7-224. Washington, 1951.

2171. Urbanski, Todeusz. Chemistry and technology of explosives, v. 1, 2, 3. Warszawa, Polish Scientific Publishers, 1967. Translated by Jurecki, Martin, New York, Pergamon Press.

PROFILE REPORT

Diazodinitrophenol (DDNP) (521)

1. GENERAL

Diazodinitrophenol (DDNP, Dinol, 2-diazo-1-oxy-4,6-dinitrobenzene) is a yellow or reddish-yellow amorphous powder. It is prepared by diazotizing picramic acid, $NH_2(NO_2)_2C_6H_2OH$, with sodium nitrite and hydrochloric acid. The dark brown, granular product obtained is thoroughly washed with ice water and is purified by dissolving in hot acetone and precipitating by the addition of a large volume of ice water. Diazodinitrophenol is almost insoluble in water and alcohol, and is stored under water or under an alcohol-water mixture.

Diazodinitrophenol is as sensitive to impact as mercury fulminate, but less sensitive to friction. Its sensitivity to friction is approximately that of lead azide, whereas it is more sensitive to heat than either mercury fulminate or lead azide. This makes for ease of ignition and thereby renders it slightly more adaptable for use than lead azide. It is considerably more stable than mercury fulminate, but not as stable as lead azide. Like lead azide, diazodinitrophenol has largely replaced mercury fulminate in commercial blasting caps and to some extent in ammunition.[0474,1147,1433,2171]

Chemical/physical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Diazodinitrophenol is of unknown toxicity and a Threshold Limit Value (TLV) has not been established.[0766] It is a compound containing nitrogroups and exposure should be limited. Compounds containing nitrogroups cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure, central nervous system depression, and in large quantities coma and respiratory paralysis.[0766] Diazodinitrophenol has a low vapor pressure which indicates it probably would not enter the body through inhalation, but its solubility in organic solvents indicates it may enter the body through skin absorption.

3. OTHER HAZARDS

Diazodinitrophenol is a primary initiating explosive that is so sensitive to electrical discharge, heat, friction, and impact that it undergoes detonation when subjected to a very mild electrical, mechanical or thermal shock from a spark, flame or percussion. It has approximately the same sensitivity to friction as lead azide. The explosion temperature value is 180 C. It detonates when struck a sharp blow, but it burns with a flash, if ignited, when unconfined and even in quantities of several grams. However, even slight confinement causes the transition of burning into detonation.[1147] Water effectively desensitizes diazodinitrophenol; it is not detonated by a No. 8 blasting cap when wet with water.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

In addition to excess diazodinitrophenol, waste wash water and acetone-water used for the recrystallization of diazodinitrophenol will contain some diazodinitrophenol that will require treatment. After evaporation of acetone in the purification process, the residues must be kept wet until treated. Diazodinitrophenol collected from wash water sumps must also be kept wet until destroyed.

The sensitivity of diazodinitrophenol to shock and friction requires that it be packaged for storage or shipment in a wet condition. If shipment or storage under low temperature conditions is anticipated, a mixture of equal weights of water and ethanol is used. Packaging is accomplished by placing approximately 25 lb, wet with not less than 20 percent liquid in a duck-cloth or rubberized-cloth bag, covered with a cap of the same material. The bag is then tied securely. Not more than six such bags are placed in a larger bag of the same material. The larger bag is tied and placed in the center of a watertight metal or wooden barrel, drum, or keg lined with a heavy close-fitting jute bag. The large bag containing diazodinitrophenol is surrounded with well-packed sawdust that has been saturated with water or water-ethanol mixture. The bag forming a liner is sewn closed before closing the barrel, drum, or keg. Not more than 150 lb of diazodinitrophenol is permitted in a single container.[1147]

Diazodinitrophenol is shipped wet under the Department of Transportation (DOT) regulations for an Explosive, Class A. It is covered by DOD regulations for an explosive with a sensitivity of Class 9, Group M.[0474,1147]

Because diazodinitrophenol is a sensitive high explosive, it is recommended that no diazodinitrophenol be released to the environment. Provisional limits have not been established for DDNP. The waste forms containing DDNP are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap, explosive, and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes - cardboard, paperboard, fiberboard, and the like). The quantities by location of DDNP, and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV, title "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of diazodinitrophenol are briefly described in the following paragraphs together with recommendations as to adequacy. Detailed discussions of the processing operations are presented in the referenced diazodinitrophenol disposal reports. Because of the explosive hazard, it is recommended that the responsible disposal engineer become acquainted in detail with explosive disposal operations before attempting to dispose of diazodinitrophenol. Under no circumstances should waste diazodinitrophenol, or materials contaminated with DDNP be handled dry, or by anyone other than an experienced disposal team.

Option No. 1 - Detonation

When more than a few pounds of diazodinitrophenol are to be destroyed, detonation is the usual current disposal procedure. Wet diazodinitrophenol is transported to the disposal area. Then several bags are removed from the transporting container (described in Section 4.), carried to the destruction pit, placed in intimate contact with each other, and blasting caps are placed between the bags to initiate the diazodinitrophenol. Remaining explosives must be kept behind a barricade with overhead protection during the destruction operations and located at a distance that assures safety. Personnel must be behind a similar barricade.[1147,2168,2170,2230] This destruction process which liberates NO_x is only satisfactory for small quantities of diazodinitrophenol. If large quantities are to be destroyed, the NO_x liberated can cause an environmental problem. Detonation is not recommended as a disposal procedure for DDNP unless safety considerations rule out transportation and handling for disposal via Option 3.

Option No. 2 - Treatment with Sodium Hydroxide

Small quantities of diazodinitrophenol such as residues left on parts can be decomposed to an unknown but non-explosive substance by adding the water-wet material to 100 times its weight of 10 percent sodium hydroxide. Nitrogen gas is evolved.[0474, 1147] The remaining residue, though not identified in the publications referenced, requires isolation and development of a method for destruction such as neutralization and solvent extraction, followed by incineration.

Option No. 3 - Controlled Incineration

The controlled slurry incineration technique currently being developed under Army cognizance is recommended for disposal of waste DDNP. In the process, a 1 to 3 slurry of DDNP in water is fed to a rotary kiln incinerator equipped with suitable afterburner or alkaline scrubbing systems for the the abatement of the NO_x liberated. If the alkaline scrubbing approach is employed for NO_x abatement, the scrubber liquid effluent (essentially a purge or bleed-off from a recirculating system) is neutralized and diluted to where the combined nitrite and nitrite contents are below 250 ppm.

Option No.4 - Detonator Destruction/Deactivation Furnace Incineration

The method approved by the Armed Forces for the disposal of detonators, primers, blasting caps, and disassembled small arms ammunition containing DDNP and other primary initiating explosives is by burning or detonation in a specially designed detonator furnace.[2170] In this furnace the components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dust and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent lead and copper pollution as detailed under the Profile Reports for lead and copper.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of detonators and primers containing DDNP. Detonators and primers from the disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metal components of the primers and detonators are recovered as scrap.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The manufacture and use of diazodinitrophenol is limited to those plants involved in the manufacture of commercial blasting caps and ammunition. Such plants have facilities for the disposal of diazodinitrophenol in waste streams, as scrap, or as excess material. DDNP waste and DDNP contaminated wastes from commercial operations which are not disposed of at such facilities are candidates for National Disposal Sites if the specific waste can be handled and transported safely. All DDNP wastes and DDNP contaminated wastes should be transported wet, in a vehicle properly equipped for the safe transport of high explosives, and only to the nearest satisfactory disposal area. The disposal process recommended for use with DDNP wastes other than blasting caps and ammunition at National Disposal Sites is the controlled incineration technique of Option 3, above. If DDNP contaminated wastes other than blasting caps and ammunition are to be disposed of and they are not capable of being handled as a slurry, the decontamination approach of Option 2 should be employed. DDNP wastes and DDNP contaminated wastes should only be handled by a qualified ordnance team, experienced in handling DDNP. If the disposal team considers the handling and transportation to a National Disposal Site of any DDNP waste would cause undue hazard to the team or the public, the waste should be destroyed by detonation in a cleared area.

Commercial blasting caps and ammunition, if safe to transport, should be deactivated by the techniques of Option 4.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of DDNP, after disassembly of the military ordnance devices, should be that of Option 4 above.

7. REFERENCES

0474. Tomlinson, W. R., Jr. revised by O. E. Sheffield. Properties of explosives of military interest, Technical Report No. 1740, Rev. 1, Picatinny Arsenal, Apr. 1958. 348 p.

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corporation, 1968. 1,251 p.

2171. Urbanski, Todeusz, translated by Marian Jurecki, Chemistry and technology of explosives, v III, Warszawa, Polish Scientific Publishers, 1967, translation Pergamon Press, New York. 714 p.

2230. Department of the Air Force, Explosive safety manual, AF Manual AFM127-100, Washington. Dec. 2, 1971.

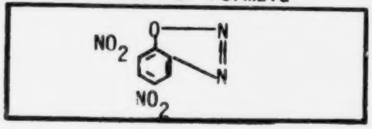
HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Diazodinitrophenol (521)

IUC Name 2-diazo-1-oxy-4,6-dinitrobenzene

Common Names

Structural Formula



Molecular Wt. 210(1)

Melting Pt. 157 C

Boiling Pt. 180 C explodes

Density (Condensed) 1.63g/cc @ 20 C

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.08g/100g at 25 C

Hot Water

Ethanol 0.84g/100g at 25

Others: 6.0g/100g acetone at 25 C

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in bags wet with water or ethanol-water

ICC Classification explosive, Class A

Coast Guard Classification Explosive, Class A

Comments Primary explosive; very highly sensitive to impact, friction, heat, and electrical shock.

References (1) 0474

PROFILE REPORT

Dinitrotoluene (165)

1. GENERAL

Dinitrotoluene (DNT) is manufactured by the stepwise nitration of toluene with mixed acid (sulfuric and nitric acids). Both the 2,4 and 2,6 isomers are produced by this process but only the 2,4 isomer is of commercial significance. Although dinitrotoluene is used in explosives and propellants, its principle uses are for the manufacture of polyurethanes and as a dye intermediate. Much of the dinitrotoluene produced is reduced to the diamine by a proprietary liquid phase catalytic process. The diamine is then reacted with phosgene to make toluene diisocyanate. In this process, all waste streams are sent to incineration.[1433] The physical/chemical properties of DNT are summarized in the attached worksheet.

2. TOXICOLOGY

Signs and symptoms attributed to dinitrotoluene toxicity are dermatitis, gastritis, and methemoglobinemia which give rise to characteristic patterms of cyanosis, aplastic anemia and toxic hepatitis. The chemical may be absorbed by inhalation and ingestion and, to a lesser extent, by skin contact. Skin contact may result in staining of the skin and can give rise to dermatitis in susceptible individuals. It may cause irritation of mucous membranes of the respiratory tract and eyes. Dinitrotoluene has a Threshold Limit Value (TLV) of 1.5 mg/M^3 (ACGIH 1968).[1142]

3. OTHER HAZARDS

Dinitrotoluene can be detonated by a very strong initiator. It may be an explosion hazard when involved in a fire. When burning, it can be extinguished by the use of water, carbon dioxide, dry sodium carbonate, or carbon tetrachloride. Fire fighting should be done by remote control. Its hazard properties are as follows[1142]:

Explosion temperature	
5 seconds	310 C
Vacuum stability	
120 C	0.04 cc/hr
Friction	
8 ft/sec	950 lb

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Dinitrotoluene is shipped in bottles, cans, metal barrels, drums and wooden barrels or kegs with liners. It is a DOD Class 2, Group D explosive.[1142] The regulations for storage and transportation of the chemical are provided by JANAF Hazard Working Group.[1142] To prevent skin and eye contact, inhalation and ingestion, personnel working with the chemical should wear protective slothing, rubber gloves and eye protective gear.

Normally only workers in a plant manufacturing or using DNT will be exposed to dinitrotoluene as a dust. For this reason, the only limit set has been the Threshold Limit Value (TLV) of 1.5 mg/M^3 for workers in plants manufacturing or handling DNT. Recommended provisional limits for dinitrotoluene in the environment are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Dinitrotoluene	0.05 ppm (0.015 mg/M^3)	.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Dinitrotoluene	0.075 ppm (mg/l)	Stokinger & Woodward Method

The quantities of dinitrotoluene wastes from explosives manufacture and from the dinitrotoluene content of obsolete conventional munitions are given in a later volume of this Final Report titled Waste Forms and Quantities. The bulk of these washes are in the form of various nitrocellulose based propellant compositions (ball-powder, etc.).

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Flow charts showing the manufacture of toluene diisocyanate from dinitrotoluene[1433] indicate that all waste streams are sent to incineration. JANAF Hazards Working Group[1142] and the Manufacturing Chemists Association (MCA)[1141] recommend that the chemical be destroyed by burning. The open burning recommended by JANAF will result in liberation of NO_x, and is, therefore, deemed unacceptable. MCA[1141] recommends two methods for incineration. In the first method, dry dinitrotoluene waste is poured onto sodium bicarbonate or a sand-soda ash mixture (90-10). The DNT and other ingredients are mixed and placed in heavy paper cartons with a large quantity of paper packing to serve as fuel. The cartons are then burned in an incinerator with an afterburner and an alkaline scrubber. In the second method, the waste containing dinitrotoluene is mixed with a solvent such as alcohol or benzene (concentration not given) and the solvent sprayed into the fire chamber of an incinerator with afterburners and an alkaline scrubber. Both of these methods are recommended as minimum environmental impact disposal techniques.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is not anticipated that National Disposal Sites will be required to handle large quantities of dinitrotoluene or waste contaminated with dinitrotoluene. However, it is anticipated that National Disposal Sites will be required to handle small quantities of explosive and propellant wastes containing dinitrotoluene which cannot be handled at conventional disposal sites. For this purpose, and ease of disposal, mixture of the DNT contaminated waste with $NaHCO_3$ and solid combustibles followed by incineration in an alkaline-scrubber equipped incinerator unit is recommended.

7. REFERENCES

1141. Manufacturing Chemists Association. Laboratory waste disposal manual. 2d ed. Manufacturing Chemists Association, Sept. 1969. 14 p.

1142. JANAF Hazards Working Group. Chemical rocket/propellant hazards. v. 2. CPIA Publication No. 194. Silver Springs, Maryland, Chemical Propulsion Information Agency, May 1970. p. 1-3.

1433. Kirk-Othmer encyclopedia of chemical technology. 2d ed. 22 v. and suppl. New York, Wiley-Interscience Publishers, 1963-1971.

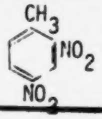
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrotoluene (165)

IUC Name 2,4-Dinitrotoluene

Common Names DNT

Structural Formula



Molecular Wt. 182.13 Melting Pt. 69.5 C Boiling Pt. 300 C

Density (Condensed) 1.521 g/cc @ 22 C Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

- @ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.02 g/100 ml @ 22 C Hot Water Ethanol 30.4 g/100 ml @ 15 C

Others: soluble in ether

Acid, Base Properties

Highly Reactive with reducing substances

Compatible with

Shipped in fiber drums, bottles, cans, metal drums

ICC Classification Explosive Class 2 Group D Coast Guard Classification

Comments

References (1) 1142

PROFILE REPORT

Dipentaerythritol-Hexanitrate (DPEHN) (522)

1. GENERAL

Dipentaerythritol-hexanitrate (DPEHN) is a white crystalline explosive used as an ingredient of priming compositions. It is present in pentaerythritol tetranitrate (PETN) as an impurity at a concentration of 2 to 3 percent. DPEHN is obtained in the pure state by fractional crystallization from moist acetone solution from which PETN has been precipitated. DPEHN can also be prepared by nitration of dipentaerythritol with nitric acid without the use of sulfuric acid.[0474]

The physical/chemical properties of DPEHN are summarized on the attached worksheet.

2. TOXICOLOGY

DPEHN has low contact toxicity since it is nearly insoluble in water. Because of its low solubility it cannot be absorbed through the skin. It is handled dry, not wet as is PETN, which makes inhalation of its dust possible. As with PETN, small quantities ingested will cause a decrease in blood pressure and larger doses could cause dyspnea and convulsions.[1147] The Threshold Limit Value (TLV) for DPEHN has not established, but should be similar to that of nitroglycerin (2 mg/cu.m).

3. OTHER HAZARDS

DPEHN is a detonating agent that is so sensitive to heat, impact, and friction that it undergoes detonation when subjected to very mild thermal, mechanical or electrical shock from a flame, an electric spark, or percussion. It explodes when heated to 255 C.[1147]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

DPEHN is stored dry in accordance with DOD regulations for a Class 9, Group M explosive and is classified by Department of Transportation (DOT) as an Explosive, Class A.

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DPEHN will be found as a waste along with PETN in wash water from PETN manufacture and in acetone-water solutions from which PETN is precipitated after its preparation. If DPEHN is manufactured by nitration of dipentaerythritol, the wash water and the acetone-water solution from which DPEHN is reprecipitated will contain DPEHN. Acetone from the acetone-water solution is recovered by evaporation and condensation. All DPEHN and PETN, if present, must be retained for destruction. Because it is a high explosive, no DPEHN should be released to the environment.

The safe disposal of DPEHN is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
DPEHN	0.02 mg/M^3*	0.01 TLV*

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
DPEHN	0.1 mg/l	Stokinger & Woodward Method

The waste forms containing DPEHN are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--cardboard, paperboard, fiberboard, and the like). The quantities by location of the DPEHN and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV of this report.

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*Estimated from data for similar compounds

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of DPEHN are briefly described in the following paragraphs, together with recommendations as to adequacy. Because of the explosive hazard, it is recommended that only personnel qualified in handling initiating agents perform the disposal operations.

Option No. 1 - Treatment with Ferrous Chloride

DPEHN as well as PETN is rapidly decomposed in a boiling solution of ferrous chloride.[1147] The products of this reaction are dipentaerythritol and ferric chloride, which are at present being diluted, neutralized, and discharged into streams. The method is satisfactory for use if the iron hydroxide and organic matter are removed via the secondary sludge sanitary waste treatment technique.

Option No. 2 - Detonation

Detonation is currently used as the disposal method when packaged DPEHN is to be destroyed. With this method several bags of DEPHN are carried to a remote destruction pit, placed in intimate contact with each other and blasting caps placed between the bags to initiate the DPEHN. Remaining explosives must be kept behind a barricade with overhead protection during the destruction operations. Personnel must be behind a similar barricade.[1174, 2170. 2230.] This process is not satisfactory for large quantities of DPEHN because NO_x will be liberated to the environment.

Option No. 3 - Controlled Incineration

Methods are currently being developed for the controlled combustion of water slurries of high explosives in rotary kiln incinerators equipped with afterburners or flue gas scrubbers. DPEHN, in the form of a 1:3 slurry in water, may be destroyed by this technique, which is recommended for use in preference to Options 1 or 2 above.

Option No. 4 - Deactivation Furnace Incineration

Small arms cartridges containing DEPHN in the primer should be disassembled from the projectile and deactivated by burning or detonation in a specially designed furnace similar to the Deactivation Furnace under development for the Chemical Agent Munition Disposal System (formerly Transportable Disposal System) by the U. S. Army Material Command. The disassembled cartridges would be fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metal components of the cartridges would be recovered as scrap.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major use of DPEHN is in priming compositions in military and sporting ammunition. Ammunition manufacturing plants and ammunition storage depots have facilities for the disposal of waste DPEHN or wastes contaminated with DPEHN. DPEHN and DPEHN-contaminated wastes from the civilian economy which are not processed for disposal at such facilities are candidate waste stream constituents for National Disposal Sites if the specific waste can be handled and transported safely. DPEHN wastes other than ammunition should be transported wet, in watertight containers. Transportation should be in a vehicle properly equipped for safe transport of primary explosives and only to the nearest satisfactory disposal site. The containers used for wet transportation must be thoroughly washed, and the wash water used for slurrying the waste DPEHN in preparation for disposal. The disposal process to be employed for wastes other than ammunition should be the controlled incineration recommended as Option No. 3 in Section 5. Surplus scrap or obsolete materials containing DPEHN should only be handled by qualified advance demolition personnel experienced in disposal of primary explosives. If hazards to the demolition team and the public are deemed excessive, the DPEHN should be destroyed by detonation in a cleared area. Sporting ammunition, if safe to transport, should be deactivated by the techniques of Option No. 4.

Obsolete military ammunition scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for deactivation after disassembly of the military ammunition should be that of Option N. 4 above.

7. REFERENCES

0474. Tomlinson, W. R., Jr., revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Rev. 1, Pictinny Arsenal, Apr. 1958. 348 p.

1147. Department of the Army and Air Force. Military explosives, TM9-1910. Washington. Apr. 1955. 336 p.

2170. Ordnance Corp., Department of the Army. Ordnance safety manual. ORDM7-224, Washington. 1951.

2230. Department of the Air Force. Explosive safety manual. AF Manual AFM127-100. Washington. Dec. 2, 1971.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dipentaerythritol-Hexanitrate (522)

IUC Name

Common Names DPEHN

Structural Formula

$C_{10}H_{16}N_6O_{19}$

Molecular Wt. 443(1) Melting Pt. 73.7 C Boiling Pt. 225 C explodes

Density (Condensed) 1.63 @ 23 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water slightly soluble Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in bag dry in a waterproof container

ICC Classification Explosive, Class A Coast Guard Classification Explosive, Class A

Comments

References (1) 0474

PROFILE REPORT

Glycol Dinitrate (525)

1. GENERAL

Glycol dinitrate, also known as ethylene glycol dinitrate, nitroglycol, and ethylene nitrate, is a colorless liquid that is used in conjunction with nitroglycerin in the manufacture of low-freezing dynamites. The sensitivity of glycol dinitrate precludes any use other than the manufacture of dynamite. It is manufactured by the use of mixed acids via the same process used to manufacture nitroglycerin (see Profile Report on Nitroglycerin [307]). The nitration can be carried out at a lower temperature because the starting material, glycol, is less viscous than glycerol, the starting material for nitroglycerin.[0474, 1142, 1433]

Glycol dinitrate is manufactured by nitrating glycol in a "mixed acid" containing about 40 percent nitric acid, 59.5 percent sulfuric acid and 0.5 percent water. After nitration of the glycol is complete, the resulting emulsion is allowed to stand in a separating tank until a supernatant layer forms which contains glycol dinitrate contaminated with nitric and sulfuric acids. This supernatant layer is separated, washed first with water, then with sodium carbonate solution and then further with water until the glycol dinitrate is neutral. Special filters are used to collect the glycol dinitrate from the waste and wash water systems.

The physical/chemical properties for glycol dinitrate are summarized in the attached worksheet.

2. TOXICOLOGY

Because of the greater volatility of glycol dinitrate, inhalation of its vapors is more of a problem than with nitroglycerin. Glycol dinitrate can cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure, central nervous system depression, coma and respiratory paralysis through inhalation, ingestion or skin absorption.[0433] The Threshold Limit Value (TLV) for glycol dinitrate is 0.2 ppm.[0225]

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3. OTHER HAZARDS

Glycol dinitrate is a powerful explosive whose decomposition into gaseous products is accompanied by the evolution of large quantities of heat and a shock wave. Glycol dinitrate is very sensitive to mechanical shock or impact, undergoing detonation under a falling weight of 1 lb at a height of 4 cm.[0474] Wastes containing glycol dinitrate should be handled only by an experienced explosives and ordnance disposal team.

4. DEFINITION OF ADEQUATE WASTE TREATMENT

Handling, Storage and Transportation

Procedures for safe handling, storage and transportation of glycol dinitrate are nearly identical to those for nitroglycerin and have been described by the JANAF Hazards Working Group.[1142] Recommended procedures for manufacturing plant layout and materials of construction, personnel requirements, manufacturing flow description, process control and disposition of waste are also included.

Glycol dinitrate, because of hazards in handling, is never transported as such beyond the plant in which it is manufactured.[1433]

Disposal of Waste Glycol Dinitrate from the Manufacturing Process

Wash waters and mixed acid nitrating solutions from the manufacturing process for glycol dinitrate are stored until all dissolved/entrained glycol dinitrate has decomposed.[1142] The spent acid is normally recovered by elevated temperature processing techniques.

The safe disposal of glycol dinitrate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Glycol dinitrate	0.02 mg/M^3*	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Glycol dinitrate	0.1 mg/l*	Stokinger and Woodward Method

The waste forms containing glycol dinitrate are for the most part scrap or surplus dynamite and manufacturing wastes composed of scrap explosive and explosive-contaminated inert combustibles such as straw, cardboard, paperboard and fiberboard. The quantities by location of the glycol dinitrate, and of the waste forms in which it is contained are included in the quantities listed under the heading "High Explosives" in the tables covering "Explosive Manufacturing Wastes" in Volume XIV of the Report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Glycol dinitrate collected from spills and catch tanks, or considered unsuitable for use (contaminated or unstable to the KI test), is disposed of by careful burning after absorption in sawdust, wood pulp or fullers earth. If glycol dinitrate is spilled on the ground, the contaminated ground is removed with low impact tools and is burned. Ignition of glycol dinitrate waste is usually accomplished by a black powder squib on the surface. All burning is performed in a remote area. Although the products of combustion contain considerable NO_x, pollution-free methods for glycol dinitrate disposal are not in wide use.[1142]

Alkali sulfides are useful as glycol dinitrate decontamination agents. Sodium sulfide, water, acetone, and methanol as a mixture is used for this purpose. A 17.5 percent sodium sulfide solution in water is sometimes used, with or without organic solvents. The glycol dinitrate is saponified and reduced by this material to insensitive compounds. This method is used with minute quantities of glycol dinitrate since the decomposition reactions are exothermic; with larger quantities, where the heat of reaction is not dissipated, there is danger of explosion due to thermal shock. The alkali sulfide method of decomposition is usually limited to cleaning equipment. This technique liberates sulfur compounds with a very disagreeable, pungent odor, along with vapor of the organic solvents used.[1142] This method is not recommended except on a very small scale.

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*Estimated from data for similar compounds.

Investigations are being conducted to develop better methods for the disposal of nitroglycerin than the open-burning techniques currently used. These methods when developed can probably be used for the disposal of glycol dinitrate. Methods showing promise are bacterial attack and controlled (scrubber-equipped) incineration, but neither of these methods are available for wide use at this time. Additional research is required.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a Deactivation Furnace which is particularly suited to the disposal of small charges of high explosive (such as dynamite). High explosives up to about 7 lb in weight per charge, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Glycol dinitrate is not normally a candidate waste stream constituent for National Disposal Sites because it is not transported as such and facilities for its disposal are available at the sites where it is manufactured. It is anticipated that a system to effect minimum impact disposal of small quantities of glycol dinitrate blended with nitroglycerin in the form of dynamite will be required at National Disposal Sites. Controlled incineration of safe lot sizes in the scrubber-equipped Deactivation Furnace incinerator is the recommended process for disposal.

7. REFERENCES

0225. American Conference of Government Industrial Hygienists. Threshold limit values for 1971. Occupational Hazards, p 35-40. Aug. 1971.

0474. Tomlinson, W.R., Jr., revised by O. E. Sheffield. Properties of explosives of military interest, Technical Report No. 1740, Rev. 1, Picatinny Arsenal, Apr. 1958. 348 p.

1142. JANAF Hazard Working Group. Chemical rocket propellant hazards: solid rocket propellant handling, processing, storage and transportation. v.2 pt.1-3. CPIA Publication No. 194, Silver Springs, Maryland. 99 p.

1433. Kirk-Othmer, Encyclopedia of chemical technology. 2 ed. 22v. and suppl. New York, Interscience Publishers. 1963 - 1971.

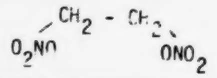
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Glycol Dinitrate (525)

IUC Name

Common Names Ethylene Glycol Dinitrate, Nitroglycol, Ethylene Nitrate

Structural Formula



$O_2NO-CH_2-CH_2-ONO_2$

Molecular Wt. 152(1)

Melting Pt. -22.8 C(1)

Boiling Pt. 257 explodes(1)

Density (Condensed) 1.489 @ 20 C

Density (gas)

Vapor Pressure (recommended 55 C and 20 C)

0.05 torr @ 20 C(1)   1.4 torr @ 60 C(1)   5.9 torr @ 80 C(1)

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.68g/100g at 20 C (1)

Hot Water 0.92g/100g at 50 C (1)

Ethanol

Others:

Acid, Base Properties

Highly Reactive with Reducing substances(1)

Compatible with

Shipped in

ICC Classification not shipped(1)

Coast Guard Classification not shipped(1)

Comments

References (1) 0474

PROFILE REPORT

Smokeless Gunpowder (541)

1. GENERAL

The term "smokeless gunpowder" is used to describe a variety of propellant (low explosive) compositions generally used in projectile weapon service. The two broad types into which these compositions fall are single base propellant and double base propellant.

All current smokeless gunpowder compositions employ nitrocellulose as the major component. As indicated by its name, single base propellant contains nitrocellulose, and a relatively small amount of additives, plasticizers, and modifying agents. Double base propellant, as currently manufactured, is composed principally of nitrocellulose and nitroglycerin, with relatively small amounts of additives, plasticizers and modifying agents. Occasionally, other explosives have been used in addition to nitroglycerin. Two characteristic smokeless gunpowder products and the processes used to manufacture them are described below.

Single base, solvent extruded propellant is colloided nitrocellulose containing about 1 percent of diphenylamine to improve its storage life and a small amount of plasticizer (e.g., dibutyl phthalate). Modifying agents such as dinitrotoluene and certain inorganic salts are sometimes added in order to reduce the flash of the gun in which the powder is used and to minimize the hygroscopicity of the powder. The colloiding is usually accomplished by pumping ethyl alcohol through the wet nitrocellulose in a hydraulic press to remove the water (this makes a drying process unnecessary), adding ether, and macerating in a dough mixer. This combination of alcohol and ether reduces the nitrocellulose to a pulpy mass that may be extruded into rope or cut to a definite length to give powder grains. The solvent is removed from the grains by heating in vats under water, and the small amount of water remaining is removed by air drying.[1147]

Ball powder is manufactured by a process whose first step is to charge nitrocellulose-in-water slurry into a still, where the NC is dissolved in ethyl acetate, stabilized with diphenylamine and neutralized with chalk. Nitroglycerin is added as a solute in the ethyl acetate fed to the still, when double base ball powder is to be produced.

The dissolved NC is dispersed into small spheres or balls by stirring under controlled conditions, adding a protective colloid (generally, animal glue) to prevent coalescence of the spheres. The solvent is boiled off and recovered, and the balls are screened into several size fractions and coated with a deterrent (such as dinitrotoluene) to control burning rate. Ball powder thus manufactured has been used interchangeably with conventional powder for loading small arms ammunition, both sporting and military, up to and including shells for 37 mm aircraft cannon. As noted in a TRW trip report (see Appendix D, Third Monthly Report) a mid-western location where ball powder had formerly been processed contained about ten million lb of finely divided ball powder wastes in process water discharge sloughs and plant sewers.

The physical/chemical properties for smokeless gunpowder are not summarized on a worksheet since smokeless gunpowder does not have a definite composition.

2. TOXICOLOGY

The toxicology of each smokeless gunpowder composition is the sum of the toxicologies of the individual components. Refer to the Profile Reports on Nitrocellulose (534), Nitroglycerin (307), and Dinitrotoluene (165).

3. OTHER HAZARDS

Smokeless powder is an explosive material which is principally a fire hazard. Its hygroscopicity requires that it be packaged in waterproof airtight containers. Smokeless powder was formerly packaged for storage in copper-lined wooden boxes, which held as much as 150 lb and were air-pressure tested for resistance to leakage before use.

Standard containers for smokeless powder are now made of stainless steel with a rubber-gasketed closure.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The management of waste from smokeless powder is not much different than that for nitrocellulose. Smokeless gun powder, because of the stabilizer additives employed in its formulation, has an extremely slow degradation rate. For this reason, smokeless gun powder wastes remain explosive and fire hazards for prolonged periods of time. Smokeless powder fines which have been discharged in plant sewer outfalls, in addition to their flammable and explosive hazard potential, can be sources of atmospheric pollution through the evolution of NO_x if anaerobic fermentations take place in the receiving water course stream beds. Open burning of recovered smokeless powder fines produces large quantities of NO_x.

Proper waste management practices must eliminate the safety hazards and the environmental hazards cited above.

Smokeless powder is stored under DOD regulations for Explosives, Class 2 or Class 2A and is shipped under Department of Transportation (DOT) regulations for Explosives, Class B. The waste forms containing smokeless powder are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes -- cardboard, paperboard, fiberboard, and the like). The quantities and locations of the smokeless powder and of the waste forms in which it is contained, are included in the quantities listed under the headings "Propellant, Nitrocellulose Base" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV titled Waste Forms and Quantities.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Smokeless powder is disposed of by the same processes as nitrocellulose (see Profile Report on Nitrocellulose [534]).

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Smokeless gunpowder is used to a major extent in loading small arms ammunition, both sporting and military, up to and including 37 mm. As indicated in Section 1 large quantities of ball powder waste (millions of pounds), both with and without dinitrotoluene added, have been found at one plant which indicates there is a probability that large quantities of smokeless gunpowder wastes require treatment. Open burning which liberates large quantities of NO_x cannot be considered a satisfactory process for disposal of smokeless gunpowder. When the processes for controlled incineration, discussed in the Profile Report on Nitrocellulose (534), are adequately developed, one of these methods should be used at National Disposal Sites for destroying smokeless powder wastes from manufacturing operations. Surplus and aged smokeless gunpowder can be reprocessed for recovery. If this is impossible or undesirable, smokeless gunpowder is a candidate for disposal at National Disposal Sites if the specific waste can be handled and transported safely. Smokeless gunpowder wastes other than obsolete munitions should be transported under water, in a vehicle properly equipped for safe transport of high explosives, and only to the nearest satisfactory disposal site. Surplus scrap or obsolete smokeless gunpowder should be handled by qualified ordnance demolition personnel experienced in the disposal of explosives. If hazards to the disposal team and public, due to handling and transportation to the nearest National Disposal Site, are deemed excessive by the demolition team, the material should be disposed of by burning in a cleared area. Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The techniques to be employed should be those indicated as acceptable controlled incineration procedures for demilitarization.

7. REFERENCES

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PROFILE REPORT

Lead Azide (529)

1. GENERAL

Lead azide is an important primary explosive. It exists in two allotropic forms: the alpha-form is orthorthombic, the beta-form is monoclinic. The crystallographically stable modification is the alpha-form. It is prepared by rapidly stirring a solution of lead acetate or lead nitrate and adding sodium azide. The beta-form is prepared by slow diffusion of sodium azide and lead nitrate solutions. This form has a tendency to revert to the alpha-form, either on standing at elevated temperature (ca 160 C), or when crystals of the beta-form are kept in water containing crystals of the alpha-form.

Lead azide, like hydrazoic acid, (Profile Report, Hydrazoic Acid, [528]) is liable to undergo oxidation and reduction reactions. It is partially decomposed by atmospheric oxygen to form free hydrazoic acid, nitrogen, and ammonia. The reaction is promoted by carbon dioxide in the air. When boiled in water, lead azide undergoes slow decomposition with the evolution of hydrazoic acid. Lead azide is completely decomposed by the action of dilute nitric or acetic acid in which sodium nitrate has been dissolved, and the products are soluble.

Lead azide detonates easily, with a high rate of propagation which is 4,500 m/sec at a density of 3.8 and 5,300 m/sec at a density of 4.6. The disadvantage of lead azide is the difficulty in igniting it with a flame. For this reason, when used as a primary explosive, it is usually mixed with lead styphnate, a substance particularly easy to ignite, or a charge of lead azide in a detonator is covered with a layer of lead styphnate. Lead azide passes very rapidly from burning to detonation. When used in very small amounts, it is therefore capable of initiating detonation in other explosives. It is suitable for use in detonators though it cannot be used in caps.[0474,1147,2169,2171]

For military use in the United States only one grade of lead azide is manufactured, dextrinated lead azide. The dextrinated material (91.5% lead azide, min.) is manufactured by precipitating lead azide from a solution containing dextrin. The dextrin acts as a binding agent for the particles precipitated. All of the mother liquid and wash waters are collected in a vat and treated as described in Section 5.[9474,2171]

The physical/chemical properties of lead azide are summarized in the attached worksheet.

2. TOXICOLOGY

Lead azide because of its low solubility, has moderate contact toxicity, but is highly toxic when ingested or inhaled, due to the ease with which it hydrolyzes. A Threshold Limit Value (TLV) for an 8-hr working day of 40-hr week has not been established by the American Conference of Government Industrial Hygienists, but a recommended maximum level for lead azide in air to be breathed is 0.2 mg/m^3.[1147] This value seems to be consistent with the TLV value for lead of 0.2 mg/m^3.[0225] Lead azide, when entering the human system through inhalation or ingestion, can produce both lead and azide intoxication (see Profile Reports on Hydrazoic Acid [528], and Lead, [233]).[0766]

3. OTHER HAZARDS

Lead azide is a primary explosive and detonating agent that is so sensitive to electrical discharge heat, impact, and friction that it undergoes detonation when subjected to very mild thermal, mechanical or electrical shock by flame percussion or electrical discharge. Old or contaminated lead azide presents an extreme hazard and must be handled with the greatest of care. Dextrinated lead azide, the standard military form, is less sensitive to impact than mercury fulminate, lead styphnate, diazodinitrophenol, tetrazene, or pure crystalline lead azide.

Because of the extreme sensitivity, and the high degree of explosive hazard, wastes containing lead azide should be handled only by an experienced explosives and ordnance disposal team. Normal procedures are to handle lead azide as a slurry in water, to minimize hazard.

Spontaneous explosions of lead azide take place during crystallization. Before attempting crystallization of lead azide, the details in the various references given throughout the report should be consulted. Applying pressure, friction, heat, flame, or electric discharge to crystals must be avoided to prevent explosions. Long contact with copper or copper-containing alloys must be avoided because a reaction takes place that produces copper azide, a substance more sensitive to explosion than lead azide. As with hydrazoic acid, lead azide is decomposed by ultraviolet light.[0474]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Dry lead azide does not react with or corrode, steel, iron, nickel, aluminum, lead, zinc, copper, tin, or cadmium. It does not affect coatings of acidproof paint. Lead azide in the presence of moisture corrodes zinc and copper. With copper, it forms the extremely sensitive and dangerous copper azide. For this reason lead azide is not loaded in direct contact with uncoated copper or its alloys; aluminum is generally used for detonator shells.[0474,1147]

Lead azide (dextrinated only) is shipped wet with water under Department of Transportation (DOT) regulations for Explosive, Class A. It is covered by Army regulations for an explosive with a sensitivity for Class 9, Group M.[0474,0766] A serious explosion hazard exists when dust particles settle out over a long time. Lead azides low solubility in water (0.02g/100g) reduces the possibility of discharging it in an aqueous solution. Suspended lead azide must be filtered out to avoid an explosion hazard. After destruction of lead azide by nitrous acid the effluents must contain less than 45 ppm of nitrate or nitrite.[0536]

The safe disposal of lead azide is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Lead azide	0.0015 mg/M^3 as Pb	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Lead azide	0.05 mg/l as Pb	Drinking Water Standard

The waste forms containing lead azide are for the most part the primer, detonator and fuze components of surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive contaminated "inert" materials. (The "inert" materials are almost always combustible wastes - cardboard, paperboard, fiberboard, and the like). The quantities by location of the lead azide and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV, titled "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of lead azide are briefly described in the following paragraphs together with recommendations as to adequacy. Detailed discussions of the processing operations are presented in the referenced lead azide disposal reports. Because of the explosive hazard, it is recommended that companies or engineers starting lead azide disposal operations visit an existing disposal unit operation to acquaint the responsible engineer with the operation prior to start-up of the proposed disposal processes.

Option No. 1 - Detonation

Detonation is the method currently employed when large to medium quantities of initiating explosives such as lead azide are to be destroyed. Bags containing small quantities of lead azide are kept wet while being transported to the demolition area. Several bags are removed from a container, carried to the destruction pit, and placed in intimate contact with each other. Blasting caps are placed between the bags to initiate the lead azide. The blasting caps are initiated by electrical current, with the operator at a safe distance, behind a barricade with overhead protection. Remaining explosives are kept behind a barricade with overhead protection during the destruction operations and located at a distance that assures safety.[1147,2168,2170] The destruction pit by necessity must be in a remote location that should assure limited hazard to the public from contamination of the atmosphere by lead. The destruction pit must be in alkaline soil or soil treated with lime to avoid leaching of lead into drainage water. This technique is viewed as unsatisfactory, unless hazards to demolition team personnel and the public,due to transportation and handling for disposal via Option No. 4 and Option No. 6,outweigh the ecological impact of lead released to the atmosphere by the detonation technique.

Option 2 - Treatment with Sodium Hydroxide

Lead azide may be destroyed chemically by mixing it with at least five times its weight of a 10 percent sodium hydroxide solution. The mixture is allowed to stand 16 hours and the supernatant solution containing sodium azide is decanted. The sodium azide solution is disposed of by draining into the ground.[0474,1147] The lead is precipitated and can be recovered (see Profile Report on Lead [233]). This method is extensively used for waste streams from lead azide manufacture. This procedure is not recommended unless the effluent is treated by either of the two disposal techniques listed as acceptable in the Profile Report on sodium azide (378).

Option No. 3 - Bichromate Treatment

Lead azide may be converted to potassium azide by reacting the explosive with a 10 percent solution of potassium bichromate until no more lead chromate is precipitated.[0474,1147] This method is not satisfactory for other than laboratory use with very small (milligram) quantities of lead azide.

Option No. 4 - Treatment with Nitrite

Lead azide wetted with 500 times its weight of water may be destroyed by adding to the lead azide 12 times its weight of 25 percent sodium nitrite, stirring, and then adding 14 times its weight of 36 percent nitric acid or glacial acetic acid. Aliquots of this solution are tested for complete azide destruction by testing with a ferric chloride solution; a red color indicates the presence of azide.[0474,1147] After complete destruction of the azide, the pH should be adjusted to 6.0 to 9.0 and the solution diluted to a nitrite and nitrate concentration of less than 45 ppm, the typical maximum allowable concentration in an effluent being discharged to a storm sewer, lake, or stream.[0536] Lead will be precipitated when the reaction solution is neutralized to the pH shown above. This is a satisfactory method that permits recovery of the lead, if the NO_x vapors liberated are destroyed by controlled incineration, or removed by scrubbing.

Option No. 5 - Treatment with Ceric Ammonium Nitrate

Lead azide may be decomposed by reaction with 50 times its weight of 15 percent ceric ammonium nitrate. The azide is oxidized to form nitrogen [1147] and the lead is subsequently precipitated as lead sulfate. This method though satisfactory, requires the use of a more expensive chemical than is used in the other processes described.

Option No. 6 - Electrolytic Destruction

Because about 300,000 lb of special purpose lead azide are stored in the United States, the Burlington AEC plant has developed in the laboratory a new electrolytic process. This process converts the lead azide to metallic lead and nitrogen. The lead azide is placed into solution by treatment with sodium hydroxide in an electrolytic cell with a lead cathode and a stainless steel anode. This method is recommended as most satisfactory of the options reviewed.

The reactions at the cathode and anode are as follows:

Cathode

$$Pb^{++} + 2e^- \rightarrow Pb^\circ$$

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

Anode

$$2N_3^- \rightarrow 3N_2 + 2e^-$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Option No. 7 - Detonator Destruction/Deactivation
Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of primers and detonators containing lead azide is by burning or detonation in a specially designed detonation furnace. Small arms cartridges disassembled from the projectile components can be demilitarized in a similar fashion. The explosive-containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper as pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of detonators and primers containing lead azide. Intact detonators and primers, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explsoive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major use of lead azide is as an initiating agent in military and sporting ammunition, and in detonators. Ammunition manufacturing plants and ammunition storage depots have facilities for disposal of lead azide discharged in waste streams, as scrap or as excess material.

Lead azide, and lead azide contaminated wastes from the civilian economy which are not processed for disposal at such facilities are candidate waste stream constituents for disposal at National Disposal Sites if the specific waste can be handled and transported safely. Contaminated waste or scrap azide other than military munitions and sporting ammunition should be transported wet, in a vehicle properly equipped for the safe transport of primary explosives, and only to the nearest satisfactory disposal site. The disposal process to be employed for civilian wastes other than sporting ammunition, if the material is safe for use of the technique,should be Option No.6 - electrolytic destruction. Sporting ammunition should be disassembled and deactivated in a special furnace, as per Option No. 7 above. Surplus, scrap, or obsolete lead azide and lead azide contaminated materials should only be handled by qualified ordnance demolition personnel experienced in disposal of lead azide. In the event that hazards to the disposal team and the public, due to handling and transport to the nearest disposal site, are deemed excessive or if the material is suspected in any way of contamination with copper azide, the waste should be disposed of by detonation in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of cartridge primers and detonators containing lead azide obtained by disassembly of the military ordnance devices should be that of Option No. 7 above.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Azide (529)

IUC Name Lead Azide

Common Names

Structural Formula

$Pb(N_3)_2$

Molecular Wt. 291 (1)

Melting Pt. 320 C explode (1)

Boiling Pt.

Density (Condensed) 4.38 g/ml (1) @ *25 C (1)

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.02g/100g at 18 C (1) Hot Water 0.09g/100g at 70 C (1) Ethanol insoluble (1)

Others: Ether - insoluble (1)

Acid, Base Properties

Highly Reactive with sodium hydroxide (1)

Compatible with steel, nickel, aluminum, lead (1)

Shipped in

ICC Classification Explosive A (1)

Coast Guard Classification Explosive A (1)

Comments *Dextrinated form

References (1) 1416

PROFILE REPORT

Lead 2,4-Dinitroresorcinate (LDNR) (530)

1. GENERAL

Lead 2,4-dinitroresorcinate is a less powerful explosive and a less efficient initiator than lead styphnate. It is unusually sensitive to friction or stab action without being unduly sensitive to impact; therefore, it is suitable for use as a priming material. It is prepared by treating lead nitrate in hot aqueous solution with a boiling solution of dinitroresorcinol to which a stoichiometric quantity of sodium carbonate has been added. After cooling, the precipitated lead dinitroresorcinate is washed with water, alcohol, and ether before being dried.

LDNR has the same order of sensitivity to impact as dextrinated lead azide, but it is much less sensitive to thermal shock. When lead dinitroresorcinate is exposed to a flame, it deflagrates, but does not explode with the violence of lead styphnate.

The relative difficulty involved in its manufacture and the difficulty in controlling the crystals to a small size for safe handling has limited the use of lead dinitroresorcinate. It has been used in only special designs of ammunition and in electric detonators.[0474,1433]

The physical/chemical properties for 2,4-lead dinitroresorcinate are summarized on the attached worksheet.

2. TOXICOLOGY

Lead 2,4-dinitroresorcinate is insoluble in water and organic solvents and has a very low vapor pressure which lessens the possibility of its being absorbed through the skin or by vapor inhalation. Inhalation of the dust or ingestion of LDNR should be avoided because of the possibility of lead poisoning (see Profile Report on Lead, [233]) and adverse reaction to the nitro groups. Exposure limits have not been established for lead 2-4-dinitroresorcinate.[0225,0776]

3. OTHER HAZARDS

Lead dinitroresorcinate is a primary explosive and detonating agent that is so sensitive to electrical discharge, impact, and friction that it undergoes detonation when subjected to very mild mechanical or electrical shock by percussion or electrical discharge. Because of their extreme sensitivity, and the high degree of explosive hazard, wastes containing lead dinitroresorcinate should be handled only by an experienced explosives and ordnance disposal team. Normal procedures are to handle lead dinitroresorcinate as a slurry in water to minimize hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of 2,4-dinitroresorcinate to shock and friction, as with most initiating agents, requires that all scrap and waste from preparation and purification be maintained wet for destruction. Lead, 2-4-dinitroresorcinate is packaged wet for storage and shipment. Packaging is accomplished by placing approximately 25 lb, wet with 20 percent water or a 50:50 water-alcohol mixture for low temperature storage, in a duck-or rubberized-cloth bag covered with a cap of the same material. The bag is then tied securely. Not more than six such bags are placed in a large bag of the same material. The large bag is tied and placed in the center of a watertight metal or wooden barrel, drum, or keg lined with a heavy close-fitting jute bag. The large bag containing lead 2,4-dinitroresorcinate is surrounded with well-packed sawdust that has been saturated with water or water-ethanol mixture. The bag forming a liner is sewn closed before closing the barrel, drum, or keg. Not more than 150 lb of initiating explosive is permitted in a single container. It is shipped wet under the Department of Transportation (DOT) regulations for an Explosive, Class A.[1147]

Because lead 2,4-dinitroresorcinate is a sensitive high explosive, it is recommended that no lead 2,4-dinitroresorcinate be released to the environment. The safe disposal of lead 2,4-dinitroresorcinate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Lead 2,4-dinitroresorcinate	0.0015 mg/M^3 as Pb	0.01 TLV for Pb

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Lead, 2,4-dinitroresorcinate	0.05 mg/l as Pb	Drinking Water Standard

The geographic distribution of lead 2,4-dinitroresorcinate wastes are included under the headings "Initiating Agents and Primers" in Volume XIV, titled "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No.1 - Detonation

Lead 2,4-dinitroresorcinate is usually disposed of by detonation. Wet bags in the transporting container (described in Section 4) are transported to the disposal area. Then several bags are removed from the transporting container, carried to the destruction pit, placed in intimate contact with each other, and blasting caps are placed between the bags to initiate the lead 2,4-dinitroresorcinate. Remaining explosives must be kept behind a barricade with overhead protection during the destruction operations and located at a distance that assures safety. Personnel must be behind a similar barricade.[1174,2170] The destruction pit by necessity must be in a remote location that should be located in alkaline soil or soil treated with lime in order to avoid contamination of ground water or streams with lead. Lead and NOx will be liberated to the environment. This technique is not regarded as satisfactory unless hazards to the disposal team and the public from disposal via Option 2 outweigh the ecological impact.

Option No. 2 - Controlled Combustion

The most promising technique under development for disposal of lead dinitroresorcinate and other high explosives is the controlled combustion process, which employs a rotary kiln incinerator equipped with appropriate scrubbing devices. The lead dinitroresorcinate is fed to the incinerator as a slurry in water, at a weight ratio, explosive to water, of 1:3. The scrubber effluent then requires treatment for recovery of the particulate lead oxide formed as a combustion product. This process is recommended for the disposal of lead dinitroresorcinate.

Option No.3 - Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of detonators containing lead 2,4-dinitroresorcinate is by burning or detonation in a specially designed detonation furnace. Small arms cartridges disassembled from the projected components can be demilitarized in a similar fashion. The explosive-containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper as pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of electric detonators containing lead 2,4-dinitroresorcinate. Intact detonators produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Lead dinitroresorcinate is used to a limited extent in special designs of ammunition as a primary explosive and in electric detonators. Military ammunition manufacturing plants and ammunition storage depots have facilities for disposal of lead dinitroresorcinate discharged in waste streams as scrap, or as a contaminant of other wastes.

Those wastes from the civilian economy that are not processed for disposal at such facilities are candidates for National Disposal Sites if the specific waste can be handled and transported safely. Wastes other than ammunition and electric detonators should be transported wet in a vehicle specially equipped for safe transport of primary explosives and only to the nearest disposal site. The disposal process to be employed at National Disposal Sites for wastes other than ammunition and electric detonators should be that cited as Option 2 in Section 5. Lead dinitroresorcinate and wastes contaminated with lead dinitroresorcinate should be handled only by a qualified ordnance demolition team experienced in handling lead dinitroresorcinate. If hazards to the team and the public from transportation and handling are deemed excessive by the demolition team, the waste should be disposed of by detonation in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of cartridge primers and detonators containing lead 2,4-dinitroresorcinate obtained by disassembly of the military ordnance devices, should be that of Option 3 above.

7. REFERENCES

0225. American Conference of Government Industrial Hygienist. Threshold limit values for 1971. Occupational Hazards, p. 35-40. Aug. 1971

0474. Tomlinson, W. R. Jr., revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Rev. 1, Picatinny Arsenal. Apr. 1958. 348 p.

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed., New York, Reinhold Publishing Corp. 1968. 1,251 p.

1147. Department of the Army and the Air Force. Military explosives. TM-9-1910, Washington. Apr. 1955. 336 p.

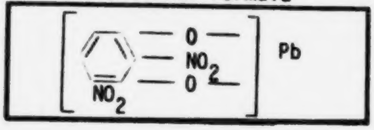
2170. Ordnance Corps, Department of the Army. Ordnance safety manual. ORDM-7-224, Washington. 1951

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead 2,4-dinitroresorcinate (530)

IUC Name Lead 2,4-dinitroresorcinate

Structural Formula



Common Names

Molecular Wt. 405(1) Melting Pt. 265 C explodes(1) Boiling Pt.

Density (Condensed) 3.2 g/cc @ 25 C (1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble(1) Hot Water Insoluble(1) Ethanol Insoluble(1)

Others: Ether-insoluble(1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags wet(1)

ICC Classification Explosive, Class A(1) Coast Guard Classification Explosive Class A(1)

Comments

References (1) 0474

PROFILE REPORT

Lead Styphnate (Lead Trinitroresorcinate) (531)

1. GENERAL

Lead styphnate or lead 2,4,6-trinitroresorcinate is used as an initiating agent in military ammunition. It is slightly less sensitive to impact than mercury fulminate or diazodinitrophenol, but is more sensitive than lead azide. It has an explosion temperature test value of 282 C which is less than that for lead azide (345 C) but much greater than those for mercury fulminate (210 C) and diazodinitrophenol (180 C). It is much more easily ignited by an electrical spark than is mercury fulminate, lead azide, or diazodinitrophenol. In spite of the fact that lead styphnate has a high rate of detonation, it is a relatively poor initiator of detonation. However, the ease of ignition of lead styphnate renders it suitable for use as an igniting charge for lead azide and as an ingredient of priming compositions. It is used extensively in the United States as an igniting charge for lead azide.[1147, 1433, 2171]

The physical/chemical properties of lead styphnate are summarized in the attached worksheet.

2. TOXICOLOGY

Lead styphnate does not have a sufficient vapor pressure to permit an appreciable concentration in air except as a dust. The toxic effects produced combine those of lead and the nitrocompounds. Organic lead compounds may be absorbed through the skin as well as through the lungs and are selectively absorbed by the central nervous system. Because of this, and the toxicity of lead (discussed in the Profile Report on Lead [233]), skin contact and areas laden with lead styphnate dust should be avoided. The amount of a lead compound in the work area should not exceed 0.15 mg of a lead compound per cubic meter for an 8-hr working day of a 40-hr week Threshold Limit Value (TLV).[0225]

3. OTHER HAZARDS

Lead styphnate is a detonating agent that is so sensitive to heat, impact, electrical discharge, and friction that it undergoes detonation when subjected to very mild thermal, electrical or mechanical shock by a flame, an electrical spark, or percussion. Because of the low solubility of lead styphnate, water may be used as a wetting agent to protect the lead styphnate from accidental explosion.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of lead styphnate to shock and friction requires that it be packaged wet, with water as the wetting agent. If it is stored or shipped under low temperature conditions, a wetting agent consisting of equal weights of ethanol and water is used. Approximately 25 lb of lead styphnate wetted with not less than 20 percent of liquid is placed for storage or shipment in a duck-cloth- or rubberized-cloth bag and covered with a cap of the same material. The bag is tied and placed in a metal or wooden barrel, drum or keg containing sawdust saturated with water or ethanol-water mixture. Not more than 150 lb of lead styphanate is permitted in a single container. Lead styphnate is classified by the Department of Transportation (DOT) as an Explosive, Class A and classified by the army as a Class 9, Group M (wet) explosive.[1147] The safe disposal of lead styphnate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Lead styphnate	0.0015 mg/M^3 as Pb	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Lead styphnate	0.05 mg/l as Pb	Drinking Water Standard

The waste forms containing lead styphnate are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive contaminated "inert" materials. (The "inert" materials are almost always combustible wastes - cardboard, paperboard, fiberboard, and the like). The quantities by location of lead styphnate wastes and the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV, titled "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of lead styphnate are briefly described in the following paragraphs together with recommendations as to adequacy. Detailed discussions of the processing options are presented in the referenced lead styphnate disposal reports. It is recommended, because of the explosive hazard, a disposal unit operation be visited to acquaint the responsible engineer with the operation before disposal operations are attempted.

Option No. 1 - Detonation

When large to medium quantities of initiating explosives such as lead styphnate are to be destroyed, detonation is the method most often used. Bags containing small quantities of lead styphnate must be kept wet while being transported to the demolition area. Several bags are removed from a container, carried to the destruction pit, placed in intimate contact with each other, and blasting caps are placed between the bags to initiate the lead styphnate. Remaining lead styphnate must be kept behind a barricade with overhead protection during the destruction operation and located at a distance that assures safety.[1147,2168,2170] The destruction pit by necessity must be in a remote location that should assure limited hazard to the public due to contamination of the environment by lead. The destruction pit must be in alkaline soil or soil treated with lime to avoid leaching of lead into drainage water. This technique is not regarded as satisfactory unless hazards to the disposal team and the public from satisfactory disposal via Option 3 or Option 5 outweigh the ecological impact.

Option No. 2 - Treatment with Sodium Dichromate

Small quantities of lead styphnate left on manufacturing equipment or in filter or wash solution are usually decomposed chemically. Lead styphnate is decomposed by first reacting it with at least 40 times its weight of a 20 percent sodium hydroxide solution or 100 times its weight of a 20 percent ammonium acetate solution. Then a 10 percent solution of sodium dichromate is added until the weight of sodium dichromate equals the weight of lead styphnate.[0474, 1147] The lead is thereby converted to insoluble basic lead chromate which is separated and disposed of in a landfill. The trinitroresorcinol formed is washed into the industrial waste drain along with any excess sodium dichromate. This process is not recommended.

Option No. 3 - Reaction with Na_2CO_3

Techniques under investigation include disposal of waste lead styphnate by reacting the material with sodium carbonate solution to yield insoluble basic lead carbonate, and an alkaline solution of trinitroresorcinol (TNR). The basic lead carbonate is separated, washed and recycled, and the trinitroresorcinol recovered for re-use in the manufacture of lead styphnate. The process is in the early development stage, and will be satisfactory if the TNR is recovered so that outfall effluents contain less than 0.5 ppm.

Option No. 4 - Reduction with NaOH and Aluminum

A current desensitization process is to react the lead styphnate with sodium hydroxide, sodium carbonate and aluminum, using live steam as a heat source. The reaction products are non-explosive and include sodium aluminate, insoluble (basic) lead carbonate, and the disodium salt of aminoresorcinol. With the exception of the lead carbonate, which is separated, the materials are discharged as a solution to the industrial waste system. The technique produces effective desensitization of the styphnate, but requires secondary treatment to destroy the aminoresorcinol, and to precipitate the aluminum.

Option No. 5 - Controlled Combustion

The most promising technique under development for disposal of lead styphnate and other high explosives is the controlled combustion process, which employs a rotary kiln incinerator equipped with appropriate scrubbing devices. The styphnate is then fed to the incinerator as a slurry in water, at a weight ratio, styphnate to water, of 1:3. The scrubber effluent would then require treatment for recovery of the particulate lead oxide formed as a combustion product. This process is recommended for disposal of lead styphnate.

Option No. 6 - Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of primers, fuzes and detonators containing lead styphnate is by burning or detonation in a specially designed detonation furnace. Small arms cartridges disassembled from the projected components can be demilitarized in a similar fashion. The explosive containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper as pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of primers, fuzes, and detonators containing lead styphnate. Intact primers, fuzes and detonators produced by disassembly of scrap munitions are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner,to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major use of lead styphnate is as an initiating agent in military ammunition. Military ammunition manufacturing plants and ammunition storage depots have facilities for disposal of lead styphnate discharge in waste streams as scrap, or as a contaminant of other wastes. Styphnate wastes from the civilian economy which are not processed for disposal at such facilities are candidates for National Disposal Sites if the specific waste can be handled and transported safely. Styphnate wastes other than munitions should be transported wet in a vehicle specially equipped for the safe transport of primary explosives, and only to the nearest disposal site. The disposal process for styphnate wastes other than munitions to be employed at National Disposal Sites should be that cited as Option No. 5 in Section 5. Styphnate wastes, and wastes contaminated with lead styphnate should be handled only a qualified ordnance demolition team experienced in handling lead styphnate. If the hazards to the team and the public from transportation and handling are deemed excessive by the demolition team, the waste should be disposed of by detonation in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of cartridge primers, fuzes and detonators containing lead styphnate obtained by diassembly of the military ordnance devices, should be that of Option No. 6 above.

7. REFERENCES

0225. American Conference of Government Industrial Hygienists. Threshold limits for 1971. Occupational Hazards, Aug. 1971. p. 35-40.

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corporation, 1968. 251 p.

1147. Department of the Army and the Air Force. Military explosives, TM9-1910. Washington, Apr. 1955. 336 p.

1433. Kirk-Othmer encyclopedia of chemical technology. 2d ed. 2 v. and suppl. New York, Interscience Publishers, 1963.

1699. Engel, R. E., D. I. Hammer, J. R. M. Horton, N. M. Lane, and L. A. Plumlee. Environmental lead and public health. Report prepared by Environmental Protection Agency, Air Pollution Control Office, Publication No. AP-90, Research Triangle Park, 1971. 34 p.

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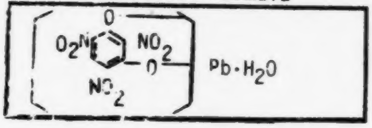
2171. Urbanski, Todeusz. Chemistry and technology of explosives, v III, Warszawa, Polish Scientific Publishers, 1967. Translated by Jurecki, Marian, New York, Pergamon Press. 714 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead styphnate (531)

IUC Name Lead 2,4,6-trinitroresorcinate

Structural Formula



Common Names Lead Styphnate

Molecular Wt 468(1) Melting Pt. 260-310 C explodes Boiling Pt. ______

Density (Condensed) 3.02g/cc @ 20 C Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water insoluble Hot Water ______ Ethanol ______

Others: glycol diacetate 0.1g/100g at 20 C

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in bag under water

ICC Classification Explosive, Class A Coast Guard Classification Explosive, Class A

Comments ______

References (1) 0474

PROFILE REPORT

Mannitol Hexanitrate (532)

1. GENERAL

D-mannitol hexanitrate, "nitromannitol," or "nitromannite" is a strong explosive with a positive oxygen balance. Its decomposition goes according to the equation:

$$C_6H_8(ONO_2)_6 \rightarrow 6CO_2 + 4H_2O + 3N_2 + O_2 + 1512 \text{ Kcal/Kg}$$

It is initiated by shock as readily as nitroglycerine. In direct contact with a flame it melts and is ignited in the open air with difficulty. Once kindled mannitol hexanitrate burns rapidly, and large quantities may explode.

Mannitol hexanitrate is manufactured by dissolving mannitol in a fivefold amount of nitric acid (d = 1.51) at a temperature below 0 C. Then a tenfold quantity of concentrated sulfuric acid (d = 1.84) is added to the solution. Fine crystals of the product are precipitated which are separated on a vacuum filter. The product is washed with cold water, neutralized by means of dilute sodium bicarbonate solution, and once again washed. Then the mannitol hexanitrate is dissolved in hot ethanol, a stabilizer, diphenylamine, added and the product crystallized.

Mannitol hexanitrate can be used as a secondary charge in some detonators, instead of tetryl. It is used in detonators in which the primary initiator is diazodinitrophenol. It has also been used in detonators with tetrazine. In addition, mannitol hexanitrate is used for medical purposes instead of nitroglycerine, since its physiological effect is slower and longer lasting.[0477,1433,2171]

2. TOXICITY

Mannitol hexanitrate can cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure, central nervous system depression and with larger quantities, coma and respiratory paralysis.[0766] Except by ingestion, it is not likely that workers will receive sufficient mannitol hexanitrate to cause a toxic reaction. The solubility in water and vapor pressure are both low and the inhalation or skin absorption of appreciable quantities of mannitol hexanitrate vapor is unlikely. Therefore, a Threshold Limit Value (TLV) has not been set for mannitol hexanitrate.

3. OTHER HAZARDS

Mannitol hexanitrate is a detonating agent that is so sensitive to heat, electrical discharge, impact, and friction that it undergoes detonation when subjected to a very mild electrical, mechanical or thermal shock from a spark, flame, or percussion.[0766] Old or contaminated mannitol hexanitrate has enhanced sensitivity and presents an extreme hazard. It must be handled with the greatest of care by an experienced ordnance disposal team.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Mannitol hexanitrate is classified by the Department of Transportation (DOT) as an Explosive, Class A and classified by the Army as a Class 9 Explosive. Its principle use is as a secondary charge in detonators and in blasting caps designed to be ignited by a fuse. It is stored dry, instead of being wet with water as are most other initiators.[0477] Because of its explosive nature, it is recommended that no mannitol hexanitrate be released to the environment. The safe disposal of mannitol hexanitrate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis Recommendation
Mannitol hexanitrate	0.02 mg/M^3	0.01 TLV*

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* Estimated from data on similar compounds.

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Mannitol hexanitrate	0.1mg/l*	Stokinger and Woodward Method*

The waste forms containing mannitol hexanitrate are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--cardboard, paperboard, fiberboard, and the like). The quantities by location of mannitol hexanitrate, and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV of this report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Detonation

The only published method for disposal of scrap mannitol hexanitrate is by detonation. Mannitol hexanitrate in small bags may be transported to the demolition area. Several bags are removed from the transporting containers and carried to a destruction pit, placed in intimate contact with each other, and a blasting cap placed between the bags to initiate the mannitol hexanitrate. All remaining explosives should be kept behind a barricade with overhead protection during destruction operations. In the destruction operation appreciable NO_x will be released per unit weight of nitromannitol destroyed. If care is taken so that only small quantities of nitromannitol are destroyed at any one time in remote locations, the NO_x produced destroying the small quantities of mannitol hexanitrate will not create an excessive environmental hazard.[1147] The safety hazards to the disposal team involved in other methods of disposal exceed the environmental impact of the NO_x released by detonation of small quantities of the material.

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* Estimated from data on similar compounds.

Option No. 2 - Open Burning

Wastes contaminated with mannitol hexanitrate are currently disposed of by open burning in a remote demolition area. The waste, if not fully combustible, is covered with fuel oil, and ignited from a safe distance using a black powder squib. The safety procedures followed are similar to those employed when detonating mannitol hexanitrate. The safety hazards to the public and the disposal team involved in other methods of disposal exceed the environmental hazard created by the release of NO_x.

Option No. 3 - Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of detonators and blasting caps containing nitromannitol is by burning or detonation in a specially designed detonation furnace. The explosive-containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper as pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of detonators and blasting caps containing nitromannitol. Intact detonators and blasting caps, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

Research is required to establish adequate procedures for the safe and minimized environmental impact disposal of nitromannitol manufacturing wastes. A tentative concept for investigation is the use of sodium sulfide solution to "kill" the nitromannitol, followed by controlled incineration of the reaction products. The incineration equipment should be provided with appropriate scrubbing devices.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The principle use of mannitol hexanitrate is as a secondary charge in detonators and in blasting caps designed to be initiated by a fuze. Except for a very small quantity that may be used in medicine, mannitol hexanitrate is stored at explosive manufacturing plants that have facilities for disposal of initiating agents. It is anticipated that waste mannitol hexanitrate will continue to be disposed of at these facilities. Nitromannitol wastes other than munitions not destroyed at the manufacturing plants are candidates for National Disposal Sites, if the specific waste is safe to handle and transport. Research is required, as noted above, to establish minimized environmental hazard procedures for the safe disposal of nitromannitol and nitromannitol contaminated wastes other than munitions. Until such procedures have been established, those cited under Options No. 1 and No. 2 of Section 5 should be used.

It should be noted that aged or contaminated nitromannitol wastes represent an unpredictable extreme disposal hazard. If at all possible, aged and contaminated wastes should be processed for disposal using remote handling devices and adequate personnel protection clothing and blast shields. In all cases nitromannitol handling and transportation for disposal should be performed only by qualified demolition personnel, experienced in disposal of nitroglycerin or nitromannitol. If the team believes handling and transportation to be sufficiently low in hazard to the team and the public, transportation should be in a special bomb disposal box, on a vehicle especially equipped for the safe transport of primary explosives and only to the nearest satisfactory disposal site. If hazards to the team and public are excessive, disposal should be by detonation or burning* in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces as National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of detonators and blasting caps containing nitromannitol after disassembly of the military ordnance devices, should be that of Option No. 3 above.

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* Using the precautions noted in Option No. 2.

7. REFERENCES

0474. Tomlinson, W. R., Jr. Revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Revision 1, Picatinny Arsenal. Apr. 1958. 348 p.

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corporation, 1968. 251 p.

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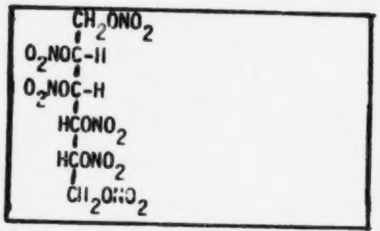
2171. Urbanski, Todeusz. Chemistry and technology of explosives, v. III, Warszana Polish Scientific Publishers, 1967. Translated by Jurecki, Marian, New York, Pergamon Press. 714 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET



$$\begin{array}{l} \quad\ CH_2ONO_2 \\ O_2NOC\text{-}H \\ O_2NOC\text{-}H \\ \quad\ HCONO_2 \\ \quad\ HCONO_2 \\ \quad\ CH_2ONO_2 \end{array}$$

H. M. Name Mannitol Hexanitrate (532)

IUC Name Mannitol Hexanitrate

Common Names

Molecular Wt. 452(1) Melting Pt. 112-113(2) **Boiling Pt.** dec. 150 C

Density (Condensed) 1.73g/cc @ 20 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Insoluble Ethanol 2.9g/100g at 13 C very soluble when hot

Others: Ether 4g/100g at 9C

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Explosive, Class A Coast Guard Classification Explosive, Class A

Comments

References (1) 0474

PROFILE REPORT

Mercuric Fulminate (Fulminate of Mercury) (533)

1. GENERAL

Mercury fulminate, $Hg(ONC)_2$, is a salt of an acid that is too unstable to exist in the free state. It is white when pure. As manufactured, the commercial product is only 98 to 99 percent pure and is grayish. $Hg(ONC)_2$ forms octahedral crystals, usually truncated, which are soluble in water to the extent of 0.01 percent at 15 C and only slightly soluble in cold ethanol. It can, therefore, be stored under water or under a mixture of equal amounts of ethanol and water to reduce the danger of explosion.

Mercury fulminate is more sensitive to impact than lead azide and lead styphnate and has the same sensitivity as diazodinitrophenol. Mercury fulminate is more sensitive to heat and friction than lead azide and lead styphnate and has a higher explosion temperature test value (210 C) than diazodinitrophenol and tetracene. The relatively poor stability of mercury fulminate is its most disadvantageous characteristic and the main reason it has largely been replaced with other initiators such as lead azide. When maintained for relatively short periods of time at 85 C, it explodes. Mercury fulminate deteriorates with age, chiefly to a nonexplosive solid rather than to gaseous products. When its purity has been reduced to about 92 percent, the initiating efficiency is practically destroyed.[0474,1147]

Mercury fulminate is manufactured in relatively small batches. Mercury is dissolved in nitric acid and this solution is poured into 90 percent ethanol, resulting in the evolution of white fumes followed by red fumes and subsequent appearance of fulminate crystals. The reaction mixture is diluted with water and the crystals repeatedly washed, by decantation, until all acid is removed.[0474,1147,2171]

The chemical/physical properties for mercury fulminate are summarized on the attached worksheet.

2. TOXICOLOGY

Mercury and its compounds are of recognized toxicity, but the handling of mercury fulminate is not unduly hazardous from a toxicity viewpoint. Because it is sparingly soluble in water, its toxicity through contact with the skin is insignificant. If taken orally, it is poisonous. Its dust should not be inhaled, and it has been recommended that the air in loading plant buildings should contain not more than 0.1 milligram of mercury fulminate per cubic meter for workers exposed for an 8-hr day five days per week.[1147]

3. OTHER HAZARDS

Mercury fulminate is a primary (initiating) explosive that is so sensitive to friction, heat, impact, and electrical discharge that it undergoes detonation when subjected to very mild thermal, mechanical, or electrical shock by flame, percussion, or electric discharge. When dry, it reacts to produce non-explosive products rapidly with aluminum and magnesium, slowly with copper, zinc, brass and bronze, and not at all with iron and steel. When wet, it reacts to produce non-explosive products immediately with aluminum and magnesium, rapidly with copper, zinc, brass and bronze and not at all with iron and steel. Mercury fulminate readily decomposes in the presence of light.[1147]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of mercury fulminate to shock and friction, as with most initiating agents, requires that all scrap and waste from preparation and purification be maintained wet for destruction. Mercury fulminate is packaged wet for storage or shipment. Packaging is accomplished by placing approximately 25 lb, wet with 20 percent water or a 50:50 water-alcohol mixture for low temperature storage, in a duck- or rubberized-cloth bag covered with a cap of the same material. The bag is then tied securely. Not more than six such bags are placed in a large bag of the same material. The large bag is tied and placed in the center of a watertight metal or wooden barrel, drum, or keg lined with a heavy close-fitting jute bag. The large bag containing mercury fulminate is surrounded with well-packed sawdust that has been saturated with water or water-ethanol mixture. The bag forming a liner is sewn closed before closing the barrel, drum, or keg. Not more than 150 lb, of initiating explosive is permitted in a single container. It is shipped wet under the Department of Transportation (DOT) regulations for an Explosive Class A.[1147] It is stored under DOD regulation for an Explosive Class 9, Group M (wet).[0474]

Waste streams from the manufacture of mercury fulminate are of three types:[2169] (1) spent liquors decanted from above the product; (2) sediment removed from the mercury fulminate by washing (slime); and (3) condensed vapors.

Waste stream (1) contains about 3 percent of dissolved material composed of 90 to 96 percent oxalic acid and 3 to 6 percent mercurous nitrate. The mercury in this stream is recovered by addition of 1 liter of hydrochloric acid to 50 liters of solution followed by the addition of zinc to precipitate metallic mercury. The mercury in waste stream (1) is sometimes recovered by the addition of lime to form a precipitate, followed by solution of the precipitate in hydrochloric acid, and recovery of metallic mercury by electrolysis or by the addition of zinc. The residual solution is treated with lime, the precipitate sent to a landfill, and the solution discharged into a sewer or stream.

Waste stream (2), slime, has a similar composition to waste stream (1) and is treated in the same manner.

Waste stream (3), condensed vapors, is chiefly ethanol and is purified for reuse by distillation over sodium.

Excess or contaminated mercury fulminate is treated in the manner described in Section 5.

Because mercury fulminate is a high explosive, it is recommended that no mercury fulminate be released to the environment outside the boundaries of a manufacturing plant. Present goals in the United States are no mercury in waste streams. It is recommended that sodium borohydride reduction and special ion exchange methods for the removal of last traces of mercury (described in Profile Report on Mercuric Cyanide, [254]) be evaluated for use on mercury fulminate manufacturing operation waste streams.

The safe disposal of mercury fulminate is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Mercury fulminate	0.0005 mg/M^3 as Hg	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Mercury fulminate	0.005 mg/l as Hg	U.S. Drinking Water Standard

The waste forms containing mercury fulminate are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--cardboard, paperboard, fiberboard, and the like). The quantities of location of the mercury fulminate, and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes," and "Obsolete Conventional Munitions" in Volume XIX, titled "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Destruction of mercury fulminate by detonation in an open burning area is a procedure employed currently for disposal[2170] which is not recommended because of the possible contamination of the environment with mercury. The recommended wet method for decomposition of mercury fulminate in manufacturing wastes is by the addition of at least 10 times its weight of a 20 percent solution of sodium thiosulfate. Some cyanogen gas may be evolved and an alkaline scrubber is required to prevent emission of $(CN)_2$.[0474,1147] The HgS precipitate obtained should be coagulated by boiling, removed by filtration, and recycled to a mercury smelter for recovery of mercury.

Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of detonators and fuzes containing mercury fulminate is by burning or detonation in a specially designed detonation furnace. Small arms cartridges disassembled from the projectile components can be demilitarized in a similar fashion. The explosive-containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NOx, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of mercury lead and copper as pollutants, as detailed under the Profile Reports for mercury lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of primers, detonators and fuzes containing mercury fulminate. Intact primers, detonators and fuzes, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization and treatment for removal of mercury, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Mercury fulminate is not at present in general use as an initiating agent. Plants manufacturing mercury fulminate for use in ammunition or detonators have facilities for the disposal of the material discharged in waste streams, as scrap, or as excess material. Mercury fulminate other than obsolete munitions which is not processed for disposal at such manufacturers' facilities is a candidate for National Disposal Sites if the specific waste involved can be handled and transported safely. The disposal process to be employed at National Disposal Sites for material other than obsolete munitions should be that recommended in Section 5 as the acceptable wet method. Surplus, scrap or obsolete materials containing mercury fulminate should only be handled by qualified ordnance demolition personnel experienced in disposal of mercury fulminate. In the event that hazards to the disposal team and the public, due to handling and transport to the nearest National Disposal Site, are deemed excessive by the demolition team, the material should be disposed of by detonation in a cleared area. Transportation of any wastes containing or contaminated with mercury fulminate should be in a vehicle properly equipped for safe transport of primary explosives, and only to the nearest satisfactory disposal site. The contaminated waste or scrap fulminate other than obsolete munitions should be transported wet.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of cartridge primers, detonators and fuzes containing mercury fulminate from obsolete military ordnance devices, should be the use of the detonator/deactivation furnace, as indicated in Section 5 above.

7. REFERENCES

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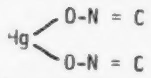
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Mercuric Fulminate (533)

IUC Name

Common Names Fulminate of mercury, mercury fulminate

Structural Formula



Molecular wt. 285 (1) Melting Pt. 210 C explodes (1) Boiling Pt.

Density (Condensed) 4.43g/cc @ 23 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C) (1)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.07g/100g at 12 C (1) Hot Water 0.18g/100g at 49 C (1) Ethanol slightly soluble (1)

Others: soluble in aqueous NH_4OH or KCN and in pyridine (1)

Acid, Base Properties

Highly Reactive with concentrated hydrochloric acid (1)

Compatible with

Shipped in

ICC Classification Explosive, Class A (1) Coast Guard Classification Explosive, Class A (1)

Comments

References (1) 3474

PROFILE REPORT

Nitroglycerin (307)

1. GENERAL

The manufacturing process and waste streams from nitroglycerin manufacture are described briefly in Section 4. Nitroglycerin is a colorless liquid, with very slight solubility in water, but miscible in all proportions with methyl alcohol, acetone, ether and benzene. Since the compound is an ester, it is hydrolyzed by alkaline solutions. It is a powerful, high brisance explosive, with marked toxicity. Chemical/physical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Nitroglycerin can cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobenemia, cyanosis, reduced blood pressure, central nervous system depression, coma and respiratory paralysis through inhalation, ingestion or skin absorption. The Threshold Limit Value (TLV) is 0.2 ppm with a skin absorption warning.[1142]

3. OTHER HAZARDS

Nitroglycerin (NG) is a powerful explosive whose decomposition into gaseous products is accompanied by a strong shock wave and the evolution of large quantities of heat. The oxygen content of the molecule is sufficient for complete oxidation of the contained carbon and hydrogen to carbon dioxide and water. Nitroglycerin is not readily flammable, but will ignite at 150 to 160 C and will explode when burning unless diluted with a considerable quantity of inert material such as fullers earth. It is very sensitive to mechanical shock or impact, undergoing detonation under a falling weight of 2 Kg at a height of 4 cm. Frozen nitroglycerin is less sensitive to impact them liquid nitroglycerin;

a half-thawed mixture, however, is more sensitive than liquid alone. Care must therefore be exercised to avoid freezing NG. If freezing does occur, extreme care must be used in thawing. Hazard properties for nitroglycerin are summarized below.[1142]

Fire

100 C heat test	
loss in first 48 hours	3.6 percent
loss in second 48 hours	3.5 percent
explosion in 100 hours	none
Explosion temperature	
5 seconds	222 C
Vacuum stability test	
90 C - cc/g - 6 hours	1.6
100 C - cc/g -16 hours	11+
Impact sensitivity, 2 Kg wt	
Bureau of Mines apparatus	15 cm
Friction (8 ft/sec)	less than 1 lb

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Procedures for safe handling, transportation and storage of nitroglycerin are described by JANAF Hazards Working Group.[1142] Their document provides recommended procedures for manufacturing plant layout and materials of construction, personnel requirements, manufacturing flow description, process control and disposition of waste nitroglycerin.

Nitroglycerin as such is not transported by common carrier because of its sensitivity to shock.

Disposal Reuse

Nitroglycerin is manufactured by nitration of glycerin in a "mixed acid" containing about 40 percent nitric acid, 59.5 percent sulfuric acid and 0.5 percent water. After nitration of the glycerin is complete, the resulting emulsion is allowed to stand in a separating tank until a supernatant layer forms which contains nitroglycerin contaminated with nitric and sulfuric acids. This supernatant layer is separated, washed first with water, then with sodium carbonate solution and then further with water until the nitroglycerin is neutral. Special filters are used so that all nitroglycerin is collected from the wash water streams. Wash waters and mixed acid nitrating solutions must be stored until all dissolved/entrained nitroglycerin has decomposed.[1142] The spent acid is normally recovered by elevated temperature processing techniques.

The safe disposal of nitroglycerin is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Nitroglycerin	0.002 ppm	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Nitroglycerin	0.1 ppm	Stokinger and Woodward Method

To make nitroglycerin easier and safer to handle it is usually converted into a different physical form such as dynamite. Modern dynamites generally use wood flour, ammonium nitrate, or sodium nitrate as an inert dilute to absorb the nitroglycerin. Such a mixture is easy to handle and can be made to contain as much as 75 percent nitroglycerin and yet retain its solid form.[1147] Other materials which contain an appreciable nitroglycerin content include ball powder, other double base gun powders, and double base rocket propellants.

The surplus double base propellants (gun powders and rocket propellants) are the major waste forms containing nitroglycerin, and occur as manufacturing wastes and as scrap conventional munitions. The quantities of these waste forms are included in those listed in Volume XIV under the heading, "Propellant, Nitrocellulose Based".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Nitroglycerin which is collected from spills and catch tanks, and that which is not considered suitable for use (contaminated or unstable to the KI test), is disposed of by careful burning after absorption in sawdust, wood pulp or fullers earth. If nitroglycerin is spilled on the ground, the contaminated ground is removed with low impact tools and is burned. Ignition of nitroglycerin contaminated waste is usually accomplished by a black powder squib on the surface. All burning is performed in a remote area. Although the products of combustion contain considerable NO_x, pollutant-free methods for nitroglycerin disposal are not in wide use.

Alkali sulfides are useful as nitroglycerin decontamination agents ("killers"). Sodium sulfide, water, acetone, and methanol mixture is used for this purpose. A 17-1/2 percent of Na_2S solution in water is sometimes used, with or without other organic solvents. The nitroglycerin is saponified and reduced by this material to insensitive compounds. This method is restricted to use with minute quantities of nitroglycerin only since the saponification and reduction reactions are exothermic; with larger quantities, where the heat of reaction is not dissipated, there is danger of explosion due to thermal shock. The alkali sulfide method of decontamination is usually limited to cleaning equipment. This technique liberates sulfur compounds with a very disagreeable, pungent odor, along with vapors of the organic solvents used. This method is therefore not recommended except on a very small scale.[1142]

In the nitroglycerin manufacturing process a mixture of nitric and sulfuric acids are used for the nitration of glycerin, and spent acid is generated as a by-product. Because the spent acid contains small quantities of dissolved nitroglycerin, it is diluted with 2 to 3 percent water to assure that the nitroglycerin is thrown out of solution. Any nitroglycerin observed on the surface of the spent acid is collected for destruction by burning after absorption in sawdust, wood pulp, or fullers earth as described above.[1142] The residual nitroglycerin dissolved in the spent acid is decomposed when the spent acid is processed for recovery.[1662]

Investigations are being conducted by the military explosive manufacturing plants (the Army Ammunition Plants) to develop better methods for the disposal of nitroglycerin than the open burning techniques currently used. Methods showing promise are bacterial attack and controlled (scrubber-equipped) incineration, but neither of these methods are available for wide use at this time. Additional research is required.

Current procedures for the disposal of manufacturing wastes such as the double base propellants are to burn a mixture of combustible inert wastes and manufacturing wastes in a safe open field or open pit. This practice is not acceptable because of the NO_X generated and emitted.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Material Command includes a deactivation furnace which is particularly suited to the disposal of small charges of dynamite, double base gun powder, and similar high explosives. High explosives up to about 7 lb in weight per charge produced by disassembly of munitions are fed via an automated conveyor to an explosion-resistant steel rotary kiln, counter-current to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end (opposite to the explosive feed end) is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner to complete oxidation of CO, and then be scrubbed in a packed tower with a solution of caustic soda or soda ash recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Nitroglycerin as the free material is not formally a candidate waste stream constituent for National Disposal Sites because it is not normally transported and facilities for its disposal are available at the sites where it is manufactured. The nitroglycerin contained in double base propellants or dynamite produced as manufacturing waste should be disposed of at the plant by an acceptable closed incineration technique similar to those under development by the Army (see above). Conventional munitions classified as surplus which contain double base propellants should be disposed of by the Armed Services at National Disposal Sites under Armed Service Cognizance, by the deactivation furnace technique covered in Section 5.

7. REFERENCES

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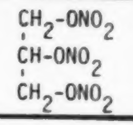
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroglycerin (307)

IUC Name

Common Names Glyceryl trinitrate

Structural Formula



$$\begin{array}{l} CH_2\text{-}ONO_2 \\ CH\text{-}ONO_2 \\ CH_2\text{-}ONO_2 \end{array}$$

Molecular Wt. 227.09 (1)   Melting Pt. 13.5 C (1)   Boiling Pt. decomposes at 50-60 C

Density (Condensed) 1.5918 @ 25 C(1)   Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

2 torr @ 125 C (1)   50 torr @ 180 C   explodes @218 C

Flash Point 218 C (1)   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water 0.12%   Hot Water 0.246% at 60 C   Ethanol 0.48%

Others: miscible with ether, acetone

Acid, Base Properties On standing with water produces 0.002% acid in 10 days

Highly Reactive with reducing substances

Compatible with

Shipped in Requires special handling; cannot be shipped by common carrier

ICC Classification cannot be shipped by common carrier   Coast Guard Classification prohibited

Comments

References (1) 1142

PROFILE REPORT

PETN (Pentaerythritol Tetranitrate) (319), TNT (418)

1. GENERAL

Both PETN (pentaerythritol tetranitrate) and TNT (2,4,6-trinitrotolene) are noninitiating high explosives and are therefore included in a combined Profile Report. Noninitiating explosives require initiation by a primer train containing initiating agents to detonate. PETN is used as a booster in military ordnance devices, and TNT is used as a high explosive fill and bursting charge in munitions, and in blasting and demolition ordnance.

PETN

PETN is a white crystalline high brisance explosive whose manufacture is described by the following equations:

$$8HCHO + 2CH_3CHO + Ca(OH)_2 \rightarrow 2C\,(CH_2OH)_4 + Ca\,(CHOO)_2$$

$$C(CH_2OH)_4 + 4HNO_3 \rightarrow C(CH_2ONO_2)_4 + 4H_2O$$

In the preparation formaldehyde and aceteldehyde are dissolved in water containing suspended slaked lime. If agitation is carried out several times a day the reaction goes to completion in about three weeks. At the end of this time, the solution is filtered. The calcium content is removed by precipitation with oxalic acid and filtration. The water is removed by evaporation under reduced pressure. On cooling, the concentrate crude pentaerythritol crystallizes. The crude material is purified by recrystallization from an alcohol-water solution. The pentaerythritol is then nitrated with strong white nitric acid at 5 C or below. The product is washed free of acid, filtered, and recrystallized from acetone. The principal uses for PETN are in detonating fuses, in boosters, and in priming compositions.[0474, 1147]

TNT

TNT is a light yellow solid high explosive used in bombs, shells, demolition charges, depth charges, and grenades. It is manufactured by sequential nitration of toluene to mono-, di, and tri-nitrotoluene. Two processes are currently in use; batch and continuous nitration. Both employ mixtures of nitric and sulfuric acid. A mixture of weak (55 percent) nitric acid with sulfuric acid is reacted with toluene to make mononitrotoluene. The crude mono-derivative is reached with slightly stronger HNO_3, mixed with H_2SO_4, at 90 to 100 C in the next stage. In the final nitration step, oleum (with 15 percent free SO_3) and 98 percent HNO_3 are reacted with the "dinitrotoluene" to form crude TNT. The crude TNT is broken up, washed free of acid, and freed of the asymmetric isomers by reaction with dilute $NaHSO_3$ solution.[0474,1157]

The physical/chemical properties for PETN and TNT are summarized on the attached worksheets.

2. TOXICOLOGY

Although PETN is not considered very toxic, the symptoms produced by ingestion are similar to those of the other aliphatic nitrates. These are dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure and central nervous systems depression. PETN is absorbed slowly from the gastrointestinal tract and the lung, but not to any appreciable extent from the skin. Safety measures to prevent explosions of PETN are sufficient to prevent undue health effects among workers.[1142] The Threshold Limit Value (TLV) for PETN has not been established.

Signs and symptoms for TNT toxicity are dermatitis, gastritis, methemoglobinemia which give rise to characteristic patterns of cyanosis, aplastic anemia, and toxic hepatitis. TNT may be absorbed by inhalation and ingestion and to a lesser extent by skin contact. Skin contact results in staining of the skin and can give rise to dermatitis in susceptible individuals. TNT may cause irritation of mucous membranes of the respiratory system and the eyes.[1142] TNT has a TLV of 1.5 mg/M^3 and may be absorbed through the skin.[0225] Low concentrations of TNT in water (>3 ppm) have an objectionable red color.

3. OTHER HAZARDS

Although both PETN and TNT are high explosives that normally require initiation by a primary explosive to detonate they may detonate when subjected to a flame or percussion. The explosion temperatures for the two explosives are given below:[1142]

PETN

Seconds	Temperature, C
0.1	272
1	244
5	225 (decomposes)
10	211

TNT

Seconds	Temperature, C
0.1	570
1	520
5	475
10	465

130 C for 100 hours - no decomposition

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The explosive character of TNT and PETN imposes the requirement that where recovery is not practical, waste streams from their manufacture and waste explosives from military and civilian ordnance devices be treated as described in Section 5. Manufacturing wastes and surplus and obsolete military munitions are the two major waste forms containing PETN and TNT. The quantities of PETN and TNT contained in these waste forms are included in the amounts listed under the "high Explosive" heading in Volume XIV titled "Waste Forms and Quantities".

PETN is shipped wet with at least 40 percent by weight of water in metal barrels, drums or kegs in which the material is packed in cloth or rubber bags. It is classified by the Department of Transportation (DOT) as a Class A explosive and is classified by DOD as a explosive Class 7, Group M. PETN is stored in a wet form. TNT is shipped as a Class A explosive. It represents an explosion hazard in case of fire but not in case of an accident without fire. TNT can be stored in a dry condition. It is classified by DOD as an explosive Class 7, Group 1,[1142] and by DOT as a Class A explosive.

The safe disposal of PETN and TNT is defined in terms of the recommended provisional limits in the environment. These are:

Contaminant in Air	Provisional Limit	Basis for Recommendation
PETN	0.02*	0.01 TLV*
TNT	0.015	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
PETN	0.1*	Stokinger and Woodward Method
TNT	0.075	Stokinger and Woodward Method

---

* Estimated from data on analogous compounds

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Chemical Destruction of PETN

Small quantities of PETN can be dissolved in acetone, and decomposed by reaction with a concentrated aqueous solution of sodium sulfide. The technique employed is to add a hot (80 C) 33 percent solution of $Na_2S \cdot 9H_2O$ to an 11 percent solution of PETN in acetone at such rate that the acetone does not boil. Seven parts by weight of sulfide solution are used per part PETN. Stirring is continued for 30 minutes after mixing is completed.[0474] The reaction products should be burned in a spray injection type incinerator equipped with a caustic soda solution scrubber. The technique is acceptable for small quantities of manufacturing waste, and for decontamination of equipment.

Option No. 2 - Chemical Destruction of TNT

TNT is decomposed by adding it slowly, while stirring to thirty times its weight of a solution prepared by dissolving one part of sodium sulfide ($Na_2S \cdot 9H_2O$) in six parts of water.[0474] The reaction products should be incinerated in an incinerator equipped with caustic soda solution scrubbers. The technique is acceptable for small quantities of TNT.

Option No. 3 - Solution Incineration

Solutions of PETN and TNT in acetone can be incinerated readily. The explosives are dissolved in at least eight times their weight of technical acetone.[0474,1142] The solution is often burned in a shallow container; this type of burning is not recommended. It is recommended that destruction be carried out in an injection type incinerator equipped with an afterburner and a caustic soda solution scrubber. The technique is acceptable for small to moderate quantities of explosives, and for decontaminating equipment.

Option No. 4 - Controlled Incineration - Manufacturing Wastes

The Army Ammunition Plants are currently investigating controlled incineration processes for the disposal of waste high explosives and high explosive-contaminated wastes. The systems under investigation include a conveyor-fed municipal type incinerator equipped with an afterburner, cyclones and wet scrubbers and a slurry-fed rotary kiln incinerator equipped with particulate abatement and wet scrubbing devices. Disposal systems of these types, when developed, will be considered acceptable for use where recovery is not feasible economically, or where contaminated inert wastes must be destroyed.

Option No. 5 - Controlled Incineration - Military Munitions

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of small charges of high explosive (such as PETN and TNT). High explosives up to about 7 lb in weight per charge, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

Option No. 6 - Open Burning

The current procedure employed for the disposal of the bulk of PETN and TNT manufacturing wastes is open burning in a safe area. This practice is not acceptable.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

PETN and TNT, and explosive contaminated wastes produced as manufacturing wastes should be disposed of at the plant site by the technique of Option Nos. 3 or 4 above, in accordance with the character and quantity of the explosive scrap involved. Conventional munitions classified as surplus which contain PETN or TNT should be disposed of by the Armed Services at National Disposal Sites under Armed Service cognizance, by the technique of Option No. 5 above. Unit operations capability for the disposal of small quantities of non-military wastes containing PETN and TNT should be provided at National Disposal Sites other than those under military cognizance. The techniques to be employed should be those of Option Nos. 3 and 4.

7. REFERENCES

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1142. JANAF Hazards Working Group. Chemical rocket propellant hazards. CPIA Publication No. 194, VII. Silver Spring, Maryland, May 1970.

1147. Department of the Army and the Air Force. Military explosives, TM-9-1910, Apr. 1958. 336 p.

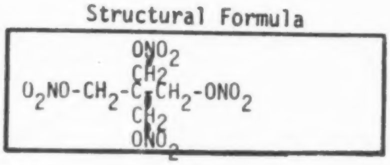
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name PETN (319)

IUC Name Pentaerythritol Tetranitrate

Common Names

Structural Formula



$$\begin{array}{c} ONO_2 \\ CH_2 \\ O_2NO-CH_2-C-CH_2-ONO_2 \\ CH_2 \\ ONO_2 \end{array}$$

Molecular Wt. 316 (1) Melting Pt. 141C (1) Boiling Pt.

Density (Condensed) 1.77 g/CC @ 20 C (1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp. 272 C explodes

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble (2) Hot Water Insoluble (2) Ethanol 0.195g/100 g at 200C

Others: Soluble-acetone, benzene, TNT (1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in metal barrels, drums or kegs (wet) (1)

ICC Classification Explosive Class "A" (1) Coast Guard Classification Explosive Class "A" (1)

Comments DOD Storage Class 7, Group M (1)

References (1) 1142

(2) 0474

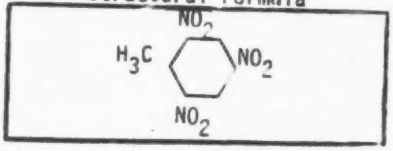
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name TNT (418)

IUC Name Trinitrotoluene

Common Names

Structural Formula



Molecular Wt. 227(1) Melting Pt. 81 C(1) Boiling Pt.

Density (Condensed) 1.65 g/cc @ 20 C (1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.042 torr @ 80 C (1) 0.067 @ 90 C (1) 0.106 @ 100 C (1)

Flash Point Autoignition Temp. 570 C explodes (1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble(2) Hot Water Insoluble(2) Ethanol 1.25g/100g at 20C

Others: Soluble - acetone, toluene, carbon tetrachloride(1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Explosive Class "A" (1) Coast Guard Classification Explosive Class "A" (1)

Comments

References (1) 1142
(2) 0474

PROFILE REPORT

Picric Acid (Trinitrophenol-Liquid)(338)

1. GENERAL

Picric acid or 2, 4, 6-trinitrophenol is manufactured as bright yellow crystals, which exist in two polymorphic forms. It was first used as a yellow dye. About 1885, military use as an explosive charge in artillery and motor shells commenced. Picric acid was the first high explosive used for meltloading. It was used widely until the beginning of this century, when it was replaced with TNT. Picric acid is used today in the United States chiefly for the manufacture of Explosive D, ammonium picrate, and in medicine and analytical chemistry.

Since it is a poly-substituted phenol, picric acid is chemically active, although less so than phenol. It decomposes carbonates and reacts with hydroxides to form picrates. Many of the picrates are more sensitive to explosion than picric acid. For military use it is stored dry, but when wet with 10 percent water picric acid may be shipped by common carrier in a maximum quantity of 16 oz per outside package.

Picric acid is manufactured by a number of processes. Direct nitration of phenol is not practical because of the violence of the reaction and consequent low yields. Phenol and sulfuric acid react to form ortho and para-phenol sulfonic acid which can be nitrated to picric acid. Another manufacturing process involves the conversion of dinitrochlorobenzene into dinitrophenol, with subsequent nitration of the dinitrophenol. A catalytic process for preparation of picric acid from benzene has been used which involves refluxing benzene with nitric acid in the presence of mercuric nitrate. Purification of crude picric acid is effected by washing with cold water, followed by recrystallization from hot water.[0472,1147]

The physical/chemical properties for picric acid are summarized on the attached worksheet.

2. TOXICOLOGY

Picric acid has a strong staining action on the human skin, but is not as toxic as some of the comparable nitro-compounds. Its dust should not be inhaled, and frequent baths and changes of clothing are prescribed for workers in production and use of picric acid.[1147] The Threshold Limit Value (TLV) for picric acid has been established as 0.1 mg per cubic meter.[0225]

3. OTHER HAZARDS

Picric acid is a high explosive that normally requires initiation by a primer but may undergo detonation when subjected to a flame or percussion. It is slightly more sensitive than TNT. The explosion temperature test value for picric acid (322 C) is lower than that of TNT (520 C).

The picrates of lead and zinc are formed by contact of molten picric acid with the appropriate metal, and are sufficiently sensitive to the thermal shock from the melt that they initiate detonation of the picric acid. Other metallic picrates are readily formed and generally contain water of crystallization. Although not as sensitive as lead picrate these picrates are very sensitive to impact when dehydrated. For this reason, formation of the picrates of iron, nickel, zinc, copper, etc. is avoided.[1147]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The explosive character of picric acid requires that all waste streams from its manufacture be treated as described in Section 5. Picric acid, dry, is classed by Department of Transportation (DOT) as an Explosive, Class A . Special regulations for picric acid wet with 10 percent water permit shipment of 16 oz maximum in an outside container by common carrier including passenger aircraft.[1147]

The safe disposal of picric acid is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Picric Acid	0.001 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Picric Acid	0.005 mg/L	Stokinger and Woodward Method

The major sources of wastes containing picric acids are the wastes from manufacturing operations, and surplus and obsolete conventional munitions scheduled for disposal by the Armed Services. The quantities and locations of picric acid in manufacturing wastes and surplus and obsolete conventional munitions are included in the quantities listed under the heading "High Explosives" in Volume XIV of this Final Report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Chemical Decomposition

Picric acid in aqueous waste streams or excess picric acid is decomposed by dissolving the material in 25 times its weight of water containing 1 part sodium hydroxide and 21 parts hydrated sodium sulfide. The hydrogen sulfide and ammonia liberated must be absorbed or scrubbed from the vent air.[0474,1147] The solution from the disposal process should be neutralized, and the phenolic material remaining oxidized by chlorine or removed by adsorption on carbon. This disposal technique is considered satisfactory where the quantity of picric acid is too low to make recovery economically attractive, or when small quantities of the material are contaminated.

Option No. 2 - Controlled Incineration-Manufacturing Wastes

The Army Ammunition Plants are currently investigating controlled incineration processes for the disposal of waste high explosives and high explosive-contaminated wastes. The systems under investigation include a conveyor-fed municipal type incinerator equipped with an afterburner, cyclones and wet scrubbers and a slurry-fed rotary kiln incinerator equipped with particulate abatement and wet scrubbing devices. Disposal systems of these types, when developed, will be considered acceptable for use where recovery is not feasible economically, or where contaminated inert wastes must be destroyed.

Option No. 3 - Controlled Incineration-Scrap Munitions

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U.S. Army Materiel Command includes a Deactivation Furnace which is particularly suited to the disposal of small charges of high explosive (such as ammonium picrate). High explosives up to about 7 lb in weight per charge, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer.

Option No. 4 - Open Incineration

The majority of picric acid wastes from manufacturing operations are disposed of by open burning in a safe area. This practice is not satisfactory because of the nitrogen oxides emitted.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The picric acid and picric acid-contaminated inert wastes produced as manufacturing wastes should be disposed of at the plant site by Options 1, 2, or 3 of Section 5 above, in accordance with the quantity and character of explosive scrap involved. Conventional munitions classified as surplus which contain picric acid as explosive fill should be disposed of by the Armed Services at National Disposal Sites under Armed Service cognizance, by the technique of Option 3, above. Small quantities of picric acid wastes from non-military sources should be disposed of at National Disposal Sites other than those under Armed Service cognizance by the techniques of Option 2.

7. REFERENCES

0225. American Conference of Government Industrial Hygienists. Threshold limit values for 1971. Occupational Hazards, p. 35-40, Aug. 1971.

0474. Tomlinson, W. R., Jr., revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Rev. 1, Picatinny Arsenal. Apr. 1958. 348 p.

1147. Department of the Army and the Air Force. Military explosives, TM-9-1910, Washington. Apr. 1958. 336 p.

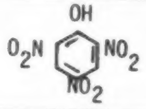
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Picric Acid (338)

IUC Name 2,4,6-Trinitrophenol

Common Names

Structural Formula



Molecular Wt. 229(1) Melting Pt. 122 C(1) Boiling Pt. 320 C explodes(1)

Density (Condensed) 1.76g/cc @ 23 C (1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

2 torr @ 195 C (1) 50 torr @ 255(1) C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1.17g/100g at 20 C(1) Hot Water 7.1g/100g at 100 C(1) Ethanol 6.9g/100g(1)

Others: Benzene 9.6g/100g(1)

Acid, Base Properties Weak acid(1)

Highly Reactive with Bases; forms sensitive metal picrates with lead, zinc, and other base metals.(1)

Compatible with

Shipped in Bottles, wet(1)

ICC Classification Explosive, Class A(1) Coast Guard Classification Explosive, Class A(1)

Comments Special regulation for common carrier(1)

References (1) 0474

PROFILE REPORT

Potassium Dinitrobenzfuroxan(KDNBF)(536)

1. GENERAL

KDNBF is the potassium salt of 4,6-dinitrobenzfuroxan and normally occurs as golden orange plates which explode at 210 C. KDNBF is used as a primary initiating explosive. First step in the preparation is the reaction of o-nitroaniline and alkaline sodium hypochlorite to produce benzfuroxan. The benzfuroxan is then dissolved in 6 parts of 96 percent sulfuric acid and nitrated at 5 to 20 C with a 4 to 1 sulfuric-nitric acid mixture. The salt is prepared by neutralization of the 4,6-dinitrobenzfuroxan. The product is purified by recrystallization from hot water.[0474]

The physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

KDNBF is not considered very toxic, but since it is an aromatic nitro-compound and is somewhat soluble in water, inhalation and skin contact must be avoided. Continued skin contact or ingestion will probably cause a decrease in blood pressure and large doses could cause dyspnea and convulsions. A Threshold Limit Value (TLV) has not been established for KDNBF.[0225]

3. OTHER HAZARDS

KDNBF is a primary initiating explosive that is so sensitive to heat, impact, and friction that it undergoes detonation when subjected to very mild thermal or mechanical shock by flame or percussion. It explodes when heated to 210 C.[0474]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

KDNBF is stored dry and handled in accordance with DOD regulations for a Class 9, Group M Explosive and is classified by the Department of Transportation (DOT) as an Explosive, Class A.[0474] Waste KDNBF is found in recrystallization and wash waters which are collected in sumps and evaporated. The recovered KDNBF is packaged for disposal as required for a Class 9, Group M Explosive.[2170,2230]

Provisional limits for KDNBF have not been established.

The waste forms containing KDNBF are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--cardboard, paperboard, fiberboard, and the like.) The quantities by location of the KDNBF and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV titled, "Waste Forms and Quantities".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Detonation has been used as the disposal method for packaged KDNBF. With this method several bags of KDNBF are carried to a remote destruction pit, placed in intimate contact with each other, and blasting caps placed between the bags to initiate the KDNBF. Remaining explosives must be kept behind a barricade with overhead protection during the destruction operations. Personnel must be behind a similar barricade.[1174,2170,2230] This process is satisfactory only for small quantities of KDNBF but provides a potential NO_x pollution problem when large quantities are detonated.

Option No. 1 - Controlled Incineration of Manufacturing Wastes

The Army Ammunition Plants are currently investigating controlled incineration processes for the disposal of waste high explosives and high-explosive-contaminated wastes. The systems under investigation include a slurry-fed rotary kiln incinerator equipped with particulate abatement and wet scrubbing devices. Disposal systems of this type, when developed, will be considered acceptable for use where recovery is not feasible economically and the scrap KDNBF must be destroyed. The slurry proportions employed are three parts of water to one part finely divided explosive. Incinerator temperatures are maintained at about 1,200 F.

The Army is also investigating the use of conveyor-fed municipal type incinerators equipped with afterburners, cyclones and wet scrubbers for the disposal of high-explosive contaminated wastes. Disposal systems of this type when developed will be considered suitable for use on KDNBF contaminated inert wastes.

Option No. 2 - Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of detonators and primers is by burning or detonation in a specially designed detonation furnace. Small arms cartridges disassembled from the projectile components can be demilitarized in a similar fashion. The explosive-containing components are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper or pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is particularly suited to the disposal of primers, fuzes, and detonators containing KDNBF. Intact component primers, fuzes and detonators, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major use of KDNBF is as a primary explosive in military ammunition. Ammunition manufacturing plants and ammunition storage depots which manufacture and process KDNBF have facilities for disposal of KDNBF and other highly sensitive explosives. KDNBF manufacturing scrap and contaminated wastes which are not disposed of at these manufacturing plants and storage depots is a candidate for disposal at National Disposal Sites, if the specific waste can be handled safely and transported safely. The contaminated waste or scrap KDNBF from manufacturing operations should be transported wet, in a vehicle properly equipped for safe transport of primary explosives, and only to the nearest satisfactory disposal site. Surplus, scrap or obsolete materials containing KDNBF should only be handled by qualified ordnance demolition personnel experienced in the disposal of primary explosives. If hazards to the disposal team and the public due to handling and transportation to the nearest National Disposal Site are deemed excessive by the demolition team, the KDNBF should be disposed of by detonation in a cleared area.

The processes cited above under Option No. 1 are the only satisfactory processes for disposal of moderate to large quantities of manufacturing wastes containing KDNBF.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed should be that of Option No. 2 above.

7. REFERENCES

0225. American Conference of Government Industrial Hygienists. Threshold limits for 1971. Occupational Hazards, p 35-40, Aug. 1971.

0474. Tomlinson, W. R., Jr., revised by O. E. Sheffield. Properties of explosives of military interest. Technical Report No. 1740, Rev. 1, Picatinny Arsenal. Apr. 1958. 348 p.

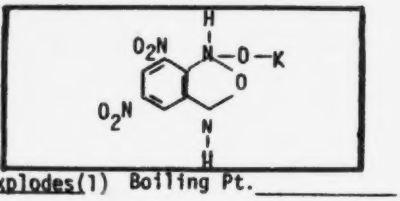
2170. Ordnance Corps, Department of the Army. Ordnance safety manual, ORD7-224. Washington. 1951.

2230. Department of the Air Force. Explosive safety manual, AF Manual AFM127-100. Washington. Dec. 21, 1971.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium dinitrobenzfuroxan (536)

Structural Formula



IUC Name

Common Names KDNBF

Molecular Wt. 267(1) Melting Pt. 210 C explodes(1) Boiling Pt.

Density (Condensed) 2.21g/cc(1) @ 23 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.245g/100g at 30 C(1) Hot Water slightly soluble(1) Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in bags(1)

ICC Classification explosive, Class A(1) Coast Guard Classification Explosive, Class A(1)

Comments

References (1) 0474

PROFILE REPORT

Primers and Detonators (520)

1. GENERAL

For purposes of this discussion, the following definitions will apply:

Primer: A primer is a small heat, impact and/or percussion-sensitive component which is charged with a single explosive mixture containing (for example) tetracene, PETN, mercury fulminate, lead azide or lead styphnate and other active or activating ingredients, which are used as first elements in explosive trains to ignite small arms propellants, black powder igniters and detonating agents. Primers will not initiate secondary high explosives reliably and do not destruct their containers when fired.

Detonator: Detonators are relatively small, sensitive explosive components which are employed to reliably initiate high order detonation in secondary high explosive charges; they can be initiated by the output of a primer or by percussion or electrical energy. Detonators are loaded with multiple charges including a primer charge and an intermediate/base charge. The primer charge materials are as mentioned above; intermediate/base charges consist of (for example) lead azide, tetryl, RDX, diazodinitrophenol (DDNP) or PETN. Detonators characteristically rupture their cases when fired.

Both the detonators and primers are generally housed in aluminum, copper, stainless or gilding metal cups. These are sealed with metal, paper or plastic at the open end.

The materials of interest from a hazardous waste standpoint are those which constitute the explosive mixture(s). As these are treated as individual compounds in other Profile Reports, the following statements will be limited to the characteristics of the materials as mixed and loaded or charged into primers and detonators.

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2. TOXICOLOGY

Primer and detonator explosive materials are relatively benign with respect to toxicology. Because the containers are sealed, the components can be considered non-toxic; ruptured or corroded containers, on the other hand, may expose the explosive materials. The toxicology of the materials may then be determined by reference to the appropriate Profile Reports.

3. OTHER HAZARDS

The explosive materials used in detonators and primers are extremely sensitive to friction, heat and impact, and undergo detonation when subjected to very mild energy input. As loaded or charged into components, the sensitivity is greatly reduced, but all handling should only be accomplished by experienced ordnance personnel. Operations involving primers and detonators should be governed by personnel safety regulations and supervised by a fully qualified safety engineer who is familiar with the characteristics of the components involved.

Older (possibly corroded) loaded components are a special case in that case-corrosion products in many instances tend to produce a marked increase in the sensitivity of certain explosive materials. In those instances in which the components are corroded, all handling should be remote-controlled and exposure of personnel minimized.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The sensitivity of the explosive mixtures used in primers and detonators generally requires that excess and scrap from charging operations be stored under water until destroyed by burning or chemical action. Primers and detonators are stored according to DOD regulations for Explosives, Group G, and shipped according to the Department of Transportation (DOT) regulations for Explosives, Class C.[2170] The waste forms containing primers and detonators are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--cardborad, paperboard, fiberboard, and the like). The quantities by location of the primers and detonators, and of the waste forms in which they are contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV of this report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Detonator Destruction Furnace

The method approved by the Armed Forces for the disposal of detonators and primers by burning or detonation in a specially designed detonator destruction furnace.[2170] In this furnace, the components are fed to the combustion chamber by means of a channel shute and a special conveying device.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a Deactivation Furnace which is particularly suited to the disposal of small charges of high explosive (including detonators and primers). Detonators and primers, obtained by disassembly of scrap munitions, are fed via an automated conveyor to an explosion resistant steel rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO, and then be scrubbed in a packed tower to remove toxic fumes and dusts such as NO_x, mercury and lead. A recirculating alkaline medium would be employed as the scrubber solution. Bleed-off from the scrubbing medium would be treated to remove mercury and lead (as indicated in the Profile Reports for mercury and lead compounds) prior to neutralization and discharge to sewer.

Option No. 2 - Burning Pit Detonation

Detonators and primers discarded as manufacturing wastes are detonated in burning pits by applying heat from a fire or by electrical ignition. The components are placed on top of flammable substances such as straw and the flammable substance is ignited by means of a squib. Other explosives must be kept behind a barricade with overhead protection during destruction operations and located at a distance that assures safety. Personnel should be similarly shielded.[1147,2170] This destruction process is not entirely satisfactory because individual components may not detonate and will constitute a personnel hazard during cleanup. Some NO_x and toxic metal particles or compounds will also be liberated during the destruction process on an uncontrolled basis.

Option No. 3 - Chemical Action

Those primers and detonators which are charged with explosive materials which can be decomposed by acids may be chemically "killed" by immersion in an acid bath of sufficient strength to destroy the seals. This method permits recovery of the metallic components as scrap, but is limited in application because the items must be segregated by explosive mixture prior to treatment.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Plants manufacturing primers and detonators have facilities for the disposal of the material discharged in waste streams, as scrap, or as excess material. Primers and detonators from the civilian segment of the economy which are not processed for disposal at the manufacturers facilities are candidate waste stream constituents for National Disposal Sites if the specific components can be handled and transported safely. The disposal process to be employed at National Disposal Sites should be Option 1, as recommended in Section 5. Surplus, scrap or obsolete materials should only be handled by qualified ordnance demolition personnel experienced in disposal or primers and detonators. In the event that hazards to the disposal team and the public due to the condition of the components or to handling and transport to the nearest National Disposal Site are deemed excessive by the demolition team, the items should be disposed of by detonation in a cleared area. Transportation of all primers and detonators should be in vehicle properly equipped for safe transport of primary explosives, and only to the nearest satisfactory disposal site.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed for destruction of the primers and detonators, after disassembly of the military ordnance devices, should be that of Option No. 1 above.

7. REFERENCES

1141. Department of the Army and the Air Force. Military explosives, TM9-1910, Washington. Apr. 1955. 336 p.

2169. Fedoroff, B. J., Encyclopedia of explosives and related items. v. 1. Picatinny Arsenal. 1960. 692 p.

2170. Ordnance Corp. Department of the Army. Ordnance safety manual, ORDM7-224. Washington. 1951.

PROFILE REPORT

Silver Azide (538)

1. GENERAL

Silver azide is a very vigorous initiator, almost as efficient as lead azide. It is slightly hygroscopic; at room temperature in a damp atmosphere it picks up approximately 2 percent water. Like lead azide, silver azide decomposes under the influence of ultraviolet irradiation. If the intensity of the radiation is sufficiently high the crystals may explode. Silver azide, AgN_3, is manufactured in the same way as lead azide, in aqueous solution, by reaction between sodium azide and silver nitrate.[2171]

Silver azide has been used to a very limited extent in this country as an initiator of explosives, but it has found use as a detonator in foreign ammunition. There is no current known manufacturer of silver azide in the United States.[0474]

The physical/chemical properties of silver azide are summarized in the attached worksheet.

2. TOXICOLOGY

Silver azide can be absorbed into the body and the silver deposited in body tissue causing greyish pigmentation of the skin, a condition known as "argyria."[2169] The Threshold Limit Value (TLV) for silver azide dust for an 8-hour day, 5 days per week has not been established, but hydrazoic acid, which may be liberated upon acidification, has a TLV of 1 mg/M^3.[0095] For a detailed discussion on the toxicology of hydrazoic acid (528) the Profile Report on this compound should be reviewed.

3. OTHER HAZARDS

Silver azide is a detonating agent that is so sensitive to heat, impact, electrical discharge, and friction that it undergoes detonation when subjected to a very mild thermal,mechanical, or electrical shock by a spark, flame or percussion. Above its melting point, 250 C, it decomposes rapidly to silver and nitrogen. When silver azide has a very fine particle size, almost colloidal, it is safer to handle and is just as efficient and resistant to hydrolysis as coarse crystalline material. White silver azide is less affected by light than mercury or lead azide. If silver azide is precipitated from ammonium hydroxide, long, colorless crystals are formed which explode on breaking.[0474]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

In handling silver azide, contact with the skin and breathing of dust particles must be avoided. Dust must not be allowed to collect because of the explosive hazard. Discharge of electric sparks must be avoided.

Silver azide is classified by Department of Transportation (DOT) as an Explosive, Class A and classified by the Army as a Class 9, Group M Explosive.[2170]

Though procedures are not published, it appears that waste silver azide can be destroyed in nearly the same manner as lead azide except that steps should be taken to recover the silver. The safe disposal of silver azide is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Silver Azide	$0.0001\ mg/M^3$ as Ag	0.01 TLV for Ag.

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Silver Azide	0.05 mg/l as Ag	Drinking Water Standard

Silver azide waste forms include scrap or obsolete foreign ammunition, and wastes from the manufacture of experimental lots of the material. The quantity of such wastes in the continental United States is not known, but is estimated to be extremely small.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Silver azide is not being manufactured at present, and therefore, specific disposal procedures have not been published. With some modification, the procedures used for the disposal of lead azide can be employed. Processes that can be used for the disposal of silver azide are briefly discussed in the following paragraphs with recommendations as to adequacy.

Option No. 1 - Detonation

The Ordnance Safety Manual recommends detonation as the best method for disposal of all initiating explosives.[2170] In the use of this procedure, bags containing the explosive should be kept wet while being transported to the demolition area. Several bags are removed from a container and carried to a destruction pit, placed in intimate contact with each other, and a blasting cap placed between the bags to initiate the explosives. All remaining explosives should be kept behind a barricade with overhead protection during destruction operations. In the use of this method, the silver present cannot be recovered, but will be lost to the soil in the demolition area. This method is not environmentally acceptable and should not be used unless the hazards of transportation and handling for disposal via the technique of Option 2 outweigh the ecological impact of detonation.

Option No. 2 - Oxidation with Nitrous Acid

Silver azide can be destroyed by oxidation with nitrous acid. This process involves wetting the silver azide with 500 times its weight of water, slowly adding 12 times its weight of 25 percent sodium nitrite, stirring, and then adding 14 times its weight of 36 percent nitric acid.[0474] Any NO_x fumes evolved should be removed by scrubbing the evolved gases with an alkaline solution. After letting the mixture stand for 16 hrs, the silver present should be recovered by electrolysis. Before discharging the silver-stripped decomposition solution, the pH should be adjusted with lime or caustic to 6.0 to 9.5 and the neutralized solution diluted to a nitrate and nitrite concentration of 250 ppm or less.

The process listed in Profile Report for disposal of lead azide (529) under Option No. 7 -- Detonator Destruction/Deactivation Furnace Incineration--is suitable for the deactivation of obsolete foreign ordnance devices containing silver azide.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Silver azide waste, and silver azide contaminated wastes from the manufacture of experimental lots of material are candidates for National Disposal Sites if the specific waste can be handled and transported safely. The silver azide waste should be transported wet, in a vehicle properly equipped for transport of primary explosives, and only to the nearest satisfactory disposal site. The disposal process to be employed should be Option 2 (Section 5). Silver azide wastes should be handled only by qualified ordnance demolition personnel experienced in handling either silver azide or lead azide. If hazards to the disposal team and the public from transportation to the nearest National Disposal Site are deemed too high, or if the silver azide is suspected of being contaminated with copper azide, the waste should be destroyed by detonation in a cleared area.

Scrap or obsolete foreign ordnance devices should be destroyed at a National Disposal Site by the technique given as Option No. 7 in the Profile Report on lead azide (529).

7. REFERENCES

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2170. Ordnance Corps, Department of the Army. Ordnance safety manual ORDM-224, Washington, 1951.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Silver azide (538)

IUC Name Silver azide

Common Names

Structural Formula

AgN_3

Molecular Wt. 149.9(1)

Melting Pt. 250 C (1)

Boiling Pt. 297-300 C explodes (1)

Density (Condensed) 4.8 g/ml @ 25 C (1)

Density (gas) @

Vapor Pressure (recommended 55°C and 20°C)

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 3.9×10^{-5} mg/l at 17 C (1)

Hot Water

Ethanol slightly soluble (1)

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in wet with water or 50:50 water ethanol in bags.(1)

ICC Classification explosive, Class "A" (1)

Coast Guard Classification Explosive "Class A" (1)

Comments

References (1) 2169

PROFILE REPORT

Tetrazene [4-Guanyl-1-(Nitroaminoguanyl)-1-Tetrazene]

1. GENERAL

Tetrazene is a pale-yellow, fluffy, crystalline solid that is prepared by adding sodium nitrite to a solution of 1-aminoguanidine hydrogen carbonate in dilute acetic acid at 30 C. After 24 hours the precipitated tetrazene is collected on a filter, washed thoroughly with water and alcohol, and dried at room temperature.

When exposed to a flame, tetrazene undergoes a mild explosion producing a large amount of black smoke. Its ignition temperature is much lower than that of mercury fulminate, although the two compounds have the same order of sensitivity to impact. Tetrazene does not initiate TNT or tetryl, but detonates uncompressed PETN. The ease of ignition, high heat of explosion, and the large volume of gaseous products given off during explosion give tetrazene its practical value as an ingredient for priming compositions. Tetrazene is relatively stable below 75 C but at 100 C it undergoes extensive decomposition.

The fact that tetrazene does not easily pass from burning to detonation makes tetrazene unsuitable for detonators. It is used as initiating explosive in ignition caps, where even 2 percent in the composition results in improved uniformity of percussion and friction sensitivity and makes it suitable as a sensitizer for friction compositions.[0474,1147,1433,2171]

The physical/chemical properties for tetrazene are summarized in the attached worksheet.

2. TOXICOLOGY

The toxicity of tetrazene is unknown, and no Threshold Limit Value (TLV) has been established. The material is insoluble in water, and is therefore assumed to be capable of only minor toxic effects.

3. OTHER HAZARDS

Tetrazene is an explosive that is so sensitive to electrical discharge, impact, friction and heat that it undergoes detonation when subjected to a very mild thermal, mechanical or electrical shock by a spark, flame or percussion. It has a lower explosion temperature (154 C) than most other initiating agents. It is its ease of ignition that renders it useful in priming compositions along with lead azide in explosive rivets. It is as sensitive to impact as mercury fulminate and diazodinitrophenol.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

In the manufacturing process, waste tetrazene from precipitation and washing operations is collected in settling tanks for treatment by the process described in Section 5. Excess tetrazene is also disposed of in the same manner. Waste tetrazene should be kept wet until treated.[1147,2171]

Handling, Storage, and Transportation

There is no standard grade of tetrazene for military use, but the handling and storage of tetrazene is the same as for most initiating agents. It is packaged for storage or shipment wet with water. If shipment or storage under low temperature conditions is anticipated, a mixture of equal weights of water and ethanol is used. Up to 25 lb of tetrazene is placed in a bag with 20 percent liquid. Six such tied bags are placed in a large bag and then the large bag is placed in a waterproof container along with wet sawdust. Not more than 150 lb of tetrazene is permitted in a single container.

Tetrazene is shipped wet under DOD regulations for an Explosive, Class A. It is covered by DOD regulations for an explosive with a sensitivity of Class 9K Group M.[0766,1147,2230]

Because tetrazene is a sensitive explosive, it is recommended that no tetrazene be released to the environment.

No provisional limits have been established for tetrazene. The waste forms containing tetrazene are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap, explosive and explosive-contaminated "inert" materials. (The inert materials are almost always combustible wastes-cardboard, paperboard, fiberboard, and the like). The quantities by location of tetrazene and of the waste forms in which it is contained, are included in the quantities listed under the headings "Initiating Agents and Primers" in the tables covering "Explosive Manufacturing Wastes" and "Obsolete Conventional Munitions" in Volume XIV titled Waste Forms and Quantities.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of tetrazene are briefly described in the following paragraphs together with recommendations as to adequacy. Because of the explosive hazard, it is recommended that only personnel trained in handling initiating agents perform the disposal operations.

Option No. 1 - Treatment with Steam

Tetrazene in sumps associated with its manufacture and excess wet tetrazene are usually decomposed by passing steam into water containing tetrazene crystals. As the temperature of the solution reaches the boiling point, the tetrazene decomposes with the liberation of two molecules of nitrogen per molecule of tetrazene. The products of the decomposition may be sent to a sewage treatment plant. This process is satisfactory and is recommended in all literature reviewed.[0474,1147,2230]

Option No. 2 - Treatment with Aqueous Sodium Hydroxide

On hydrolysis of tetrazene with 10 percent sodium hydroxide in water, ammonia, cyanamide and triazonitroaminoguanidine are produced. This method, though satisfactory, is not aften used because the process is more complex than the one described under Option 1. In this process, the sodium hydroxide in the reacting solution must be neutralized before discharging to a sewer.[1147]

Option No. 3 Detonator Destruction/Deactivation Furnace Incineration

The method currently approved by the Armed Forces for the demilitarization of ignition caps and other initiating devices containing tetrazene is by burning or detonation in specially designed detonation furnace. Ammunition cartridges disassembled from the projectile components can be demilitarized in a similar fashion. The cartridges/initiating devices are fed to the combustion chamber by means of a channel chute and a special conveying device. The detonator furnace should be equipped with an afterburner to abate NO_x, and cyclones and scrubbing towers for the removal of metallic dusts and fumes. The bleed-off from the recirculating scrubbing solution should be treated to prevent discharge of lead and copper as pollutants, as detailed under the Profile Reports for lead and copper compounds.

The Chemical Agent Munition Disposal System (formerly Transportable Disposal System) under development by the U. S. Army Materiel Command includes a deactivation furnace which is partcularly suited to the disposal of military devices containing tetrazene. Intact initiating devices, produced by disassembly of scrap munitions, are fed via an automated conveyor to an explosion-resistant rotary kiln, countercurrent to an oil or gas flame. The rotary kiln is equipped with steel screw flights to isolate the explosive charges from each other. The explosive charge end of the kiln is at about 500 F gas temperature; the kiln is about 25 ft in length, and the fired end opposite the explosive feed end is maintained at a gas temperature of about 1,200 F. Combustion product gas exits through a cyclone. In practice, the exit gases should go through an afterburner, to complete oxidation of CO prior to the cyclone, and then be scrubbed in a packed tower with caustic soda or soda ash solution recirculated as scrubbing medium. Bleed-off alkaline solution, after neutralization, would exit to sewer. The metallic components are recovered as scrap after discharge from the kiln.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The major use of tetrazene is as an initiating explosive in military ammunition and ordnance devices, and in commercial ignition caps and explosive bolts. Explosive and ammunition manufacturing plants, and those processing tetrazene for use in commercial devices have facilities for disposal of tetrogen discharged in waste streams, as scrap or as excess material. Tetrazene wastes which are not disposed of at the manufacturing plants are candidates for National Disposal Sites if the specific waste can be handled and transported safely. Tetrazene wastes other than obsolete munitions should be transported wet, in a vehicle properly equipped for transportation of primary explosives and only to the nearest satisfactory disposal site, the disposal process to be employed at National Disposal Sites should be Option No. 1 (Section 4). Scrap and contaminated wastes should be handled only by qualified ordnance personnel, experienced in disposal of tetrazene. In the event that hazards to the team and the public from handling and transportation to the nearest National Disposal Site are deemed excessive by the disposal team, the tetrazene waste should be destroyed by detonation in a cleared area.

Obsolete military munitions scheduled for disposal should be demilitarized and disposed of by the Armed Forces at National Disposal Sites under the cognizance of the Armed Forces. The technique to be employed should be that of Option No. 3 above.

6. REFERENCES

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0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corporation, 1968. 1,251 p.

1147. Department of the Army and Air Force, Military Explosives, TM9-1910, Washington, Apr. 1955. 336p.

1433. Kirk-Othmer encyclopedia of chemical technology. 2d ed. 22 New York, Interscience Publishers, 1963.

2171. Urbanshi, Todeusz, translated by Marian Jurecki, Chemistry and technology of explosives, V.III, Warszawa, Polish Scientific Publishers, 1967, translation Pergamon Press, New York. 714 p.

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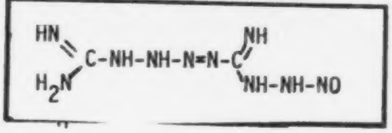
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tetrazene (542)

IUC Name 4-guanyl-1-(nitrosoaminoguanyl)-1-Tetrazene

Common Names tetracene

Structural Formula



$HN{=}C(H_2N){-}NH{-}NH{-}N{=}N{-}C({=}NH){-}NH{-}NH{-}NO$

Molecular Wt. 188.16 (1)

Melting Pt. 140-160 C explodes (1)

Boiling Pt. ____

Density (Condensed) 1.05 @ 3000 psig (1)

Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____

Autoignition Temp. ____

Flammability Limits in Air (wt %)	Lower ____	Upper ____
Explosive Limits in Air (wt. %)	Lower ____	Upper ____

Solubility

Cold Water insoluble (1)

Hot Water insoluble at 100 C decomposes (1)

Ethanol insoluble (1)

Others: insoluble, CCl_4, benzene, ether, soluble - HCl (1)

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Shipped in bags, wet

ICC Classification Explosive, Class A (1)

Coast Guard Classification Explosive, Class A (1)

Comments ____

References (1) 0474

PROFILE REPORT

Chloroacetophenone (107) Tear Gas (CN) (422)

1. GENERAL

Chloroacetophenone, also known as tear gas (CN), is a very effective solid lachrymator produced by chlorination of acetophenone or by a Friedel-Crafts reaction of benzene with chloroacetyl chloride. The chlorination of acetophenone is accomplished by direct reaction with chlorine in acetic acid solution or with selenium oxychloride in a benzene solution. In the Friedel-Crafts reaction, chloroacetyl chloride is added to benzene in the presence of aluminum chloride catalyst.[0778,1492,1662]

Chloroacetophenone is relatively stable and slow to react. It will react with most of the usual compounds that couple with the aliphatic carbonyl group such as hydroxylamine and hydrazine. However, sodium bisulfite does not react with chloroacetophenone. It is stable when exposed to detonation and has good thermal stability up to 300 C.[0788] The physical/chemical properties for chloroacetophenone are summarized in the attached worksheet.

2. TOXICOLOGY

In very low concentrations in air chloroacetophenone has an odor resembling apple blossoms. An intolerable level is considered to be 4.5 mg per cubic meter while a concentration of 850 mg per cubic meter is estimated to be lethal. The symptoms include tearing, burning of the eyes, and difficulty in breathing. The Threshold Limit Value (TLV) (ACGIH) is 0.3 mg per cubic meter (0.05 ppm).[0766] No data of the effects of chloroacetophenone on plants or aquatic life are available.

3. OTHER HAZARDS

When chloroacetophenone is heated to decomposition, it emits toxic fumes. It reacts slowly with steam to produce toxic and corrosive fumes.[0766]

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4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Though the vapor pressure of chloroacetophenone is relatively low (equilibrium concentration at 20 C is 0.11 mg/l), the vapor pressure which develops is sufficient to make a terrain contaminated with it impassible without a protective mask. The fact that chloroacetophenone does not decompose at its own boiling point makes it possible to pour the melted compound directly into shells and to mix the material with explosives such as TNT. It is a persistent lachrymator. Solutions of tear gas (CN) spread on the terrain may retain their effects for hours or days.[0778]

When working with chloroacetophenone ventilation control must be maintained. Self-contained breathing masks must be available and protective clothing and rubber gloves worn.[1141] Chloroacetophenone is shipped in glass bottles under Department of Transportation regulations for Class C poison requiring a tear gas label.[0766]

The safe disposal of CN is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Chloroacetophenone	0.003 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Chloroacetophenone	(Data on ingestion toxicity completely lacking).	

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Chloroacetophenone is expected to appear primarily as a packaged waste, in a mixture such as MACE, or with explosives whose composition is known.

Information furnished to TRW by the California Department of Justice, and a major riot control device manufacturer, indicates that there are no local government waste disposal requirements for overage and obsolete riot control devices/agents. Governmental law enforcement agencies (local) use all of the overage or obsolete devices for training exercises. There are some stocks of riot control agents of Federal (Defense) storage points scheduled for disposal. The quantities and locations of these agents are given in Volume XIV titled "Waste Forms and Quantities".

The disposal processing options are briefly described in the following paragraphs, together with recommendations as to their adequacy.

Option No. 1 - Incineration

When chloroacetophenone and mixtures of chloroacetophenone are packaged with easily combustible materials, the following process recommended by the Manufacturing Chemists Association, appears to be satisfactory.[1141] The chloroacetophenone-containing waste is dissolved in an organic solvent (usually benzene or an alcohol) and sprayed into an incinerator equipped with an afterburner and alkalie scrubber.

Option No.2 - Reaction with Sodium Sulfide

Chloroacetophenone reacts with sodium sulfide in alcoholic or alcohol-water solutions to form bis-(acetylphenyl)-thioether (melting point 74 C) which shows no physiological effect.[0778] This process is attractive because it not only converts the chloroacetophenone into a compound that has no physiological effect, but most explosive nitro compounds, when present, are decomposed to nonexplosive compounds. This process results in the liberation of hydrogen sulfide, which must be collected by an alkaline scrubber. The alcohol solution containing the decomposed compounds may be sprayed into an incinerator equipped with an alkali scrubber to remove any hydrogen chloride, nitric oxide, and sulfur oxides formed.

Option No.3 - Reaction with Sodium Thiosulfate

By boiling in an alcohol-water solution with sodium thiosulfate, the sodium salt of acetylphenyl thiosulfonic acid is obtained.[0778]

$$C_6H_5COCH_2 \cdot S_2O_3Na$$

The thiosulfonate solution must then be sprayed into an incinerator equipped with an alkali scrubber. This process converts the chloroacetophenone into a compound that shows no physiological effect, but incineration of the thiosulfonate is required. This option does not, in most cases, offer any advantages over Options No.1 and No.2.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Chloroacetophenone in small quantities as a packaged waste and as a mixture with other materials is expected to require disposal. It is anticipated that the expertise required for treating a lachrymator will not be available at the source of the waste generation. Therefore, chloroacetophenone is judged to be a candidate waste stream constituent for National Disposal Sites. Disposal processes recommended are those of Option No.1 or Option No.2.

7. REFERENCES

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1141. Manufacturing Chemists Association, Laboratory waste disposal manual. 2d ed. Washington, 1969. 161 p.

1492. Merck index of chemicals and drugs, 7th ed. Rahway, Merck Company, Inc. 1960. 1,634 p.

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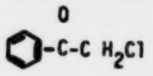
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chloroacetophenone (107)

IUC Name W-Chloroacetophenone

Common Names Phenacyl Chloride

Structural Formula



$C_6H_5-C(=O)-CH_2Cl$

Molecular Wt. 154.6(1)   Melting Pt. 58-59C(2)   Boiling Pt. 139-141 C(2)

Density (Condensed) 1.321 @ 20C   Density (gas) ____ @ ____

Vapor Pressure (recommended 55 C and 20 C)

0.012 torr @ 0   0.16 Torr @ 50 C   ____ @ ____

Flash Point ____   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water 0.1% (w/w)(2)   Hot Water ____   Ethanol Soluble (2)

Others: Soluble, ether, benzene(2)

Acid, Base Properties None

Highly Reactive with Hydroxyamine (2)

Compatible with most materials of construction

Shipped in Bottles(1)

ICC Classification Class C Poison(1)   Coast Guard Classification Class C Poison(1)

Comments

References (1) 1301
(2) 0778

ORGANOPHOSPHOROUS NERVE AGENTS

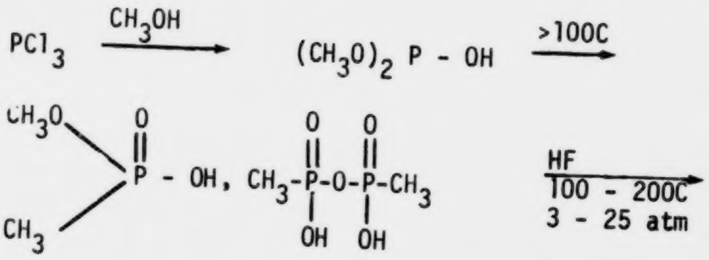
GB(287), VX(288)

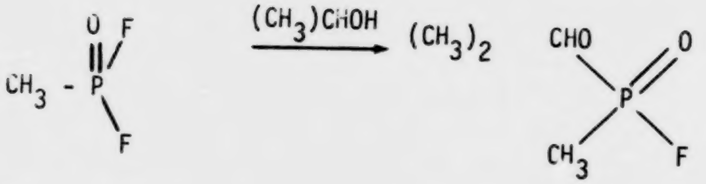
1. GENERAL

The preparation of organic phosphorus compounds dates to the last century. Over one hundred years ago tetraethyl pyrophosphate was prepared by Wurtz. The toxicity of this compound was not recognized until the 1930's. In 1932 Lange and von Krueger reported the toxic properties of a group of compounds of the class of organic phosphorus compounds. They observed that even in very minute quantities the vapors of monofluorophosphoric acid alkyl ester caused, within a few minutes of their inhalation, breathing difficulties lasting several hours, slight disturbances of the consciousness, and painful light sensitivity.

Systematic research in Germany under the direction of the IG-Farbenindustrie chemist, G. Schrader, led to the discovery of highly toxic organic phosphorus compounds. Under the strictest military secrecy, as a part of the German military chemical development program, the prerequisites for larger scale industrial production of some compounds suitable for use as chemical warfare agents were created.

GB, Propoxy (2)-methylphosphoryl fluoride was first prepared in Germany in 1938-39 as a military agent for poisoning the atmosphere, food supplies, water supply systems, etc. At the end of World War II, two plants for large scale production of this lethal agent were under construction with a combined capacity of 600 tons per month. It can be prepared by a number of techniques including the transposition method illustrated below.





GB is a colorless, odorless liquid of relatively low vapor pressure. It is hygroscopic and mixes with water in any ratio. It is thermally dissociated by heating to the vicinity of its boiling point.

VX, O-ethyl S-(2-diisopropyl aminoethyl 1) methylphosphonothioate is a member of a family of compounds of phosphoryl cholines and phosphoryl thiocholines called V agents. The V agents are a further development of the compounds synthesized and studied by Tammelin at the Swedish Research Institute of National Defense. On the basis of their extreme toxicity and militarily appropriate physical and chemical properties, the V agents are important chemical warfare agents. The techniques for the preparation of VX are classified. VX is a colorless, odorless liquid with a very low vapor pressure and is thus classified as a persistent agent.

Organic phosphorus chemical warfare agents (Table 1) are used as liquids, as sprays, and as aerosols. Long lasting contamination of the atmosphere is possible due to their volitility, their good aerosol properties and their high toxicity. Both GB and VX are usable as aerosols under all meteorological conditions. Their period of effectiveness increases with decreasing temperature. Under favorable meteorological conditions with organic phosphorus chemical warfare agents the detonation or vaporization cloud may spread up to 30 kilometers from the point of origin. Beyond that range concentrations may still be present which lead to combat incapacity.

The United States stockpiles many types of weapons which utilize organophosphorus agents. These include mortar and howitzer shells, rockets, bombs and landmines.[0778,0958] The quantity of these agents in the United States and other arsenals is classified, but it is known that over five and one-half million lb of GB are contained in M34 1000-lb bombs scheduled to be destroyed and detoxified at Rocky Mountain arsenal. [0956]

TABLE 1

SOME U.S. MUNITIONS CONTAINING ORGANOPHOSPHORUS CHEMICAL WARFARE AGENTS

Ammunition	CW Agent	Delivery Device	Ammunition Wt. Pounds	CW Agent Wt. Pounds	Explosive Wt. Pounds
Shells					
M360	GB	105mm howitzer	44	1.6	1.1
M121A1	GB/VX	155mm howitzer	100	6.5	Burster Charge
M122	GB	155 cannon	100	6.5	Burster Charge
M426	GB/VX	8in howitzer	199	14.5	Burster Charge
Rocket Warheads					
M55	GB/VX	155mm rocket	57	10.7	3.2
Bombs					
MC-1	GB	750 lb Bomb	725	220	Burster Charge
MK94	GB	500 lb Bomb	441	108	Burster Charge
Mines					
M23	VX	chemical agent mine	23	12.5	1.0
Sprayer					
TMU-28/B	VX	chemical agent spray	1935	1356	None

2. TOXICITY[0778, 0958]

The organophosphorus chemical warfare agents are powerful cholinesterase inhibitors. In their molecular structure they resemble acetylcholine and have the property of restricting and inhibiting the biocatalytic activities of the choline esterases required for the transmission of nerve impulses.

GB is a rapid acting lethal agent. The hazard from GB is primarily that of vapor absorption through a respiratory tract although it can be absorbed through any part of the skin, through the eyes and through the gastrointestinal tract by ingestion. When dispersed as large droplets, GB is moderately persistent; it is non-persistent when disseminated as a cloud of very fine particles. Skin contact with the liquid agent or inhalation of agent aerosol (or vapor) are the most common causes of exposure. The agent absorption rate is accelerated through cuts and abrasions in the skin. The results of agent exposure are as follows. The early symptoms of vapor or aerosol exposure are: (1) pinpointing of eye pupils and dimness of vision; (2) running nose; (3) tightness of chest; (4) difficulty in breathing. Early symptoms of skin contact exposure are localized sweating and muscular twitching. Later symptoms indicating severe exposure are (1) nausea and possible vomiting,(2) cramps and involuntary defecation and/or urination,(3) headache or drowsiness,(4) coma, and(5) convulsion. For a lethal dose, death occurs by heart failure.

The effects of concentration are as follows. Exposures of 2 min. to a level of 0.002 to 0.002 mg/l result in the early symptoms described above. These last for up to 4 to 5 days. A 15-min. exposure to this level of concentration may produce death. Severe intoxications, which sometimes have fatal outcome occur with concentrations of 0.005 to 0.01 mg/l with 5-min. exposure. Symptoms may last several weeks. With concentrations of 0.02 to 0.03 mg/l and an exposure time 2 to 5 min. death occurs from heart failure after 10 to 20 min. The symptoms may change with rapid succession. After a few minutes the victim becomes unconscious. The toxicity (LD_{50}) of the liquid on the skin is approximately 30 to 50 mg per kilogram of body weight.[0788] Small drops of GB on the human skin suffice to cause the early symptoms.

VX is also a lethal rapid acting nerve agent. The hazard from VX is primarily that of liquid absorption through the skin, although it can be absorbed through the gastrointestinal tract by ingestion or through the respiratory tract as a vapor or aerosol. VX is slow to evaporate and may persist as a liquid for several days. The symptoms of exposure to VX are very similar to those for GB given above, except that under severe exposure convulsion is followed by cessation of breathing and death. VX has liquid LD_{50}'s of the order of 0.03 to 0.3 mg per kilogram of body weight and are therefore 1,000 to 10,000 times more toxic than GB.

3. OTHER HAZARDS

The low volatility of GB and VX eliminates any flammable and exposure hazards from these agents. Both will decompose under severe heating to give off pollutants such as HF and H_2S. Under mild heating the vapor pressures of both agents are raised, significantly increasing the hazard of direct poisoning by the agents. Upon combustion both agents produce pollutants, GB giving HF and P_2O_5 and VX giving SO_x, NO_x and P_2O_5.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The extreme toxicity of GB and VX presents a very special challenge to the determination and utilization of adequate safety and handling procedures. The gas mask and protective clothing are designed to prevent liquid, aerosol, or vapor contact with the individual. Personal hygiene is particularly important to limiting hazards. Skin should be kept clean and dry decreasing the rate of absorption of any agent reaching the surface. Water foodstuffs, and fruits of the field must not be used before chemical examination.

Materials exposed to organophosphorus chemical warfare agents must be decontaminated before handling. They can be decontaminated by alkali hydroxides, ammonia, alkali carbonates, alkali hypochlorites, basic chloride and hydrogen peroxide. For decontamination of the ground and of streets and roads, alkali hydroxide solutions, chloride of lime suspensions, or hypochlorite solutions are used. Vehicles, technological equipment, etc., are decontaminated with hydroxide or hypochlorite solutions. Ammonia, soda, phenolate and lime solutions are used for materials which might be corroded by the strong alkali hydroxides. For decontamination of the skin and articles of personal equipment, copper (II) chelates, hydozamic acids, dilute hydrogen peroxide solutions and weak alkaline solutions can be used.

GB and VX can both be stored for extended periods in steel containers when a stabilizer such as an amine is added. Transportation of these agents is handled by the military, who utilize special sealed vans designed to contain any leakage.

Disposal/Reuse

The highly specific military application of GB and VX and their toxicity precludes their application to non-military situations in either diluted or concentrated form. Reprocessing for other military applications also does not appear practical. The safe disposal of the agents is defined in terms of the recommended provisional limits in the atmosphere. No data for marine or soil environments are available.

Contaminant in Air	Maximum Concentrations	Basis for Recommendation
GB	0.000003 mg/m^3	U.S. Army*
VX	0.000003 mg/m^3	U.S. Army*

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*Standards proposed by Surgeon General of U.S. Army for chemical demilitarization.[0958]

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Wastes

Option No.1 - Hydrolysis. Water containing wastes from the manufacture, handling or disposal of organophosphorus agents can most easily be treated using caustic soda to accelerate the hydrolysis reactions. The products of these reactions for GB and VX solutions have a much lower toxicity than the agents themselves.

GB undergoes its first reaction at the P-F bond and then at the P-O single bond. Normal reaction products are sodium fluoride and the sodium salt of methyl isopropyl phosphoric acid. Figure 1 shows the effect of pH on the half-life of GB. Specific information for VX is not available although similar compounds are known to have much slower rates of hydrolysis. The thio-choline type compounds are first attacked at the P-S bond. Quantitative conversion is possible only by the use of strong alkalies in moderately concentrated solutions. Heating of the hydrolysis mixture increases the rate at which the reactions occur. These techniques are adequate for dilute systems if agent concentration is monitored and the salt products dried and stored.

Concentrated Wastes

Option No.2 - Incineration (Transportable Disposal System). In April of 1969, the Army prepared a plan for development of a transportable system capable of disposing of any of the chemical munitions now stockpiled by the Department of Defense. Because of the presence of a large variety of chemical munitions and because of the availability of engineering personnel and shop facilities, the South Area of Tooele Army Depot was selected for test and operation of the Transportable Disposal System (TDS). The system design is based on the removal of the chemical warfare agent from the various munitions and the separate incineration of the agent, casings

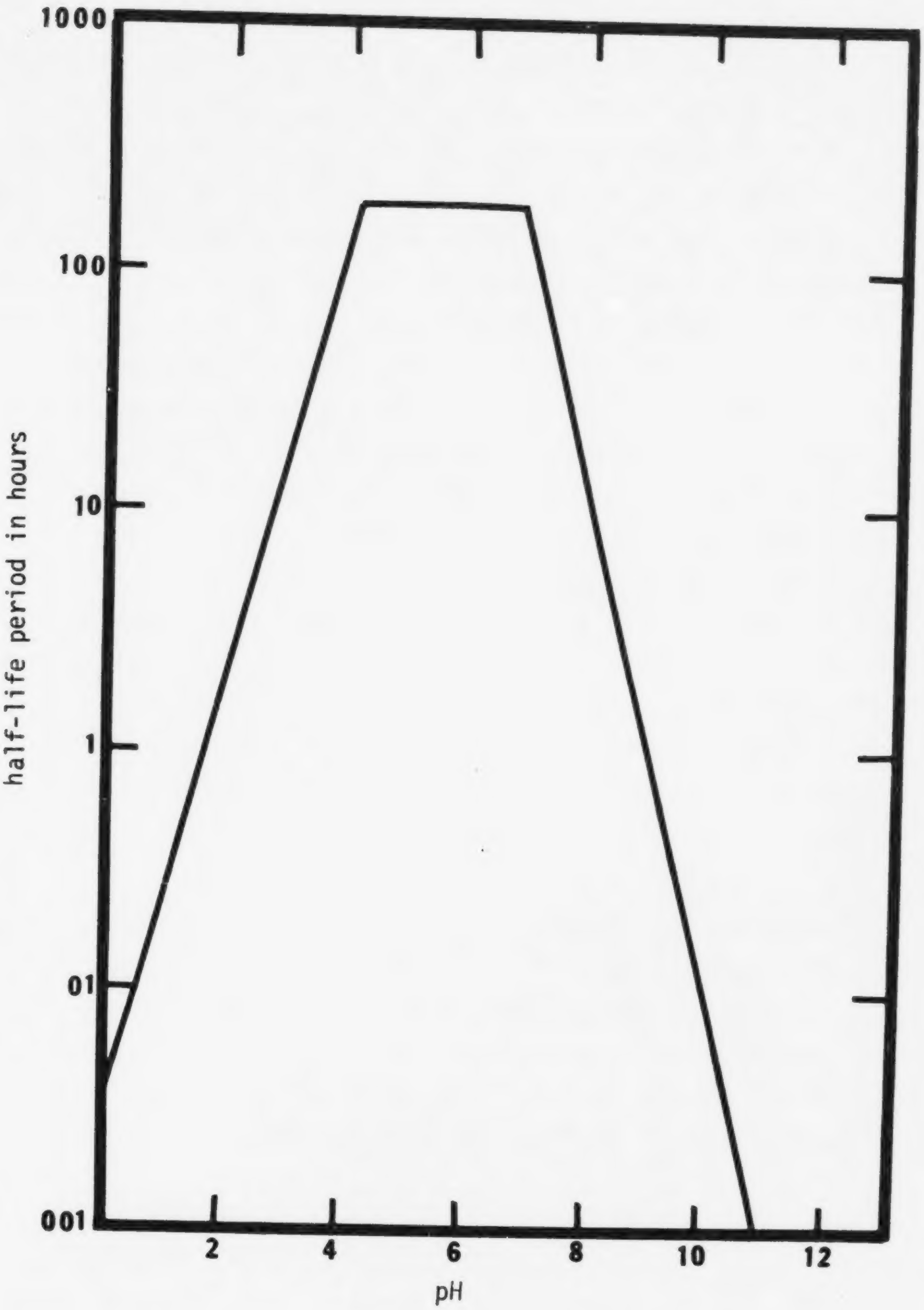


Figure 1. Hydrolysis of GB as a function of the hydrogen-ion concentration at 25 C.

and explosives and propellants. The TDS consists of twelve major subsystems: (1) Explosive Containment Cubicle (ECC) for the removal of explosives from explosive-loaded munitions; (2) Projectile Demilitarization Facility (PDF) for the removal of agents from projectiles and mortar ammunition and the decontamination of the empty hardware; (3) Bulk Item Facility (BIF) for the removal of agent from non-explosive containing bombs and ton cylinders and the decontamination of the empty hardware; (4) Deactivation Furnace (DF) for burning propellant, explosives, and empty rocket and mine bodies; (5) Deactivation Furnace Scrubbers System (DFSS) for pollution control of the effluent from the DF; (6) Metals Parts Furnace (MPF) for the thermal decontamination of empty metal parts that previously contained agents or which might have been contaminated by agent; (7) Air Pollution Control System (APCS) for scrubbing the gaseous effluent of the MPF; (8) Agent Incinerator-Scrubber System (AISS) which incinerates agent and reduces pollutant to acceptable low levels; (9) Dunnage Incinerator (DI) with scrubber used for non toxic combustibles; (10) Sludge Removal and Treatment System (SRTS) used to remove explosive materials from spent decontaminating solutions and evaporate the water; (11) Control Module (CM) which monitors and controls the above system; and (12) Personnel Support Complex (PSC) providing change rooms, locker rooms, toilet and shower facilities, lunch room and laundry.

The Agent Incinerator/Scrubber System (Table 2) is of particular importance to the disposal procedure. All agents are drained from the munitions and fed at a constant, controlled rate to the agent incinerator. The agent feed is continuously supplemented by a fuel oil flame. All incinerator controls are fail-safe and the agent feed is equipped with a fast acting cut-off valve in the event of loss of flame.

The combustion gases leaving the incinerator are water quenched before being processed through cross-flow packed scrubbers in series to remove pollutants. The scrubbing media employed in the cross-flow scrubbers are calcium hydroxide and sodium hydroxide for GB and nitric acid, sodium hydroxide and calcium hydroxide for VX incineration products.

TABLE 2

AGENT INCINERATOR/SCRUBBER SYSTEMS PARAMETERS AS CONFIGURED FOR GB

Incinerator		
Agent Feed Rate	3-6 lb/min	
Combustion Air Rate	1650 ACFM at 60F	
Fuel Oil Rate	0.36 lb/min	
Combustion Temperature	1750F	
Residence Time	>0.5 sec	
Scrubber		
Configuration	Cross flow, 2 beds in series	
Capacity	3530 ACFM at 166F	
Cross-sectional Area	1-1/2 ft wide by 6 feet high	
Stack height	50 ft	
	Bed 1	Bed 2
Length	6 ft	9 ft
Temperature	140F	80F
Liquid Flow Rate	35 gpm	140 gpm

The decontaminating solutions used in the PDF and BIF are 10 percent sodium carbonate solutions. Sodium carbonate is also the scrubbing media in the other furnace systems. All solutions are dried except the water-flyash mixture from the Dunnage Incinerator and the salts are stored. The TDS represents a very adequate disposal method which might serve as a model for pesticide and other disposal systems.

Option No. 3- Chemical Reaction. Under the auspices of Project Eagle the Army has developed a chemical detoxification procedure for the demilitarization of weapon systems containing GB. [0956] The reactions are those described earlier for the dilute wastes. Five percent excess sodium hydroxide in an 18 percent solution is reacted with GB to form sodium salts of low toxicity which are then recovered by evaporation and stored in plastic lined drums. VX may be detoxified with clorine in acidic aqueous media to give O-ethyl phosphoric acid, and diisopropylthurine hydrochloride and hydrochloric acid. This mixture is subsequently neutralized with caustic and spray dried to give the sodium salts. These salts may also be stored or used as raw material for other processes. This method is considered adequate for VX.

Option No. 4- Ocean Disposal. In the fall of 1968, the Department of the Army determined that the disposal of certain chemical munitions was necessary to remove excess and unserviceable material from our national deterrent stockpile. The proposed disposal plan (Operation CHASE) was reviewed by the National Academy of Sciences which recommended that the particular disposal should proceed as planned with certain modifications and which further recommended that ocean disposal not be used for later chemical munitions disposals. The munitions in question were sealed in concrete in blocks which were subsequently covered with steel plates which were welded. Because of their appearance, size, and shape they were called and referred to as "coffins". The coffins were shipped to a port facility, loaded on a hulk and towed out to sea. The hulk was sunk in approximately 16,000 ft of water and the area has been monitored since the disposal without any evidence of damage to the ocean ecology near the disposal site. In view of the National Academy of Science recommendation it is concluded that ocean disposal is not adequate.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The extreme toxic hazard associated with nerve agents in itself is sufficient to recommend their disposal at National Disposal Sites operated by the U.S. Army. In concern with Public Law 91-121 it is recommended that the National Site for nerve gases be the locations under military jurisdiction where these are stored. The recommended techniques are summarized below.

Process	Order of Preference	Remarks
Incineration (Transportable Disposal System)	First Choice	The TDS is specifically designed for this application and is adequately safeguarded.
Chemical Reaction	Second Choice	Salts may be stored until commercial use is defined.

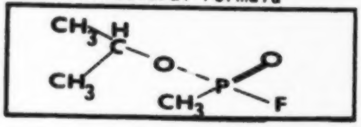
The disposal techniques discussed herein for GB and VX are presumably applicable to almost all of the organophosphorus compounds whether chemical munitions or pesticides. Special attention should be given to possible TDS modifications for application to waste pesticide and pesticide containers.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 287

IUC Name

Structural Formula



Common Names GB, Metnylisopropoxyfluoro-phosphine oxide

Molecular Wt. 140.1 Melting Pt. -56C Boiling Pt. 147C

Density (Condensed) 1.0887 g/cc @ 25 Density (gas) 4.86 @

Air = 1.

Vapor Pressure (recommended 55 C and 20 C)

1.48 mm Hg @ 20C 12 mm Hg @ 50 C 8 mm Hg @ 46 c

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water totally miscible Hot Water total Ethanol total

Others: alkanones, halogen alkanes

Acid, Base Properties

Highly Reactive with

Compatible witn

Snipped in

ICC Classification Coast Guard Classification

Comments No odor, color: straw

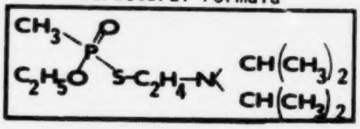
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 288

IUC Name

Common Names VX

Structural Formula



Molecular Wt. 285 Melting Pt. -39C Boiling Pt. 300C

Density (Condensed) 1.1 @ 25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

12-14mg/M^3 @ 25 C @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with Metals if stabilized by amines.

Shipped in

ICC Classification Coast Guard Classification

Comments Color: clear to straw, no odor

7. REFERENCES

0778. Franke, S. Manual of military chemistry. v. 1. Washington, Office, Assistant Chief of Staff for Intelligence, Headquarters, Department of the Army, Apr. 5, 1968. 375 p.

0956. Baronian, C., H. Johnson, D. Shearer, T. J. Sharp, and P. A. Lawrence. Office conference on ultimate disposal of chemical reaction products resulting from demilitarization of GB nerve agent at Rockey Mountain Arsenal, Colorado. Rockville, Maryland, Environmental Protection Agency, Nov. 26, 1971. 8 p.

0958. Transportable disposal system, environmental statement. Edgewood Arsenal, Department of the Army. Special Publication EASP 200-11, July 1971. 297 p.

1700. Personal communication. S. Morekas, Solid Waste Management Office, to R. S. Ottinger, TRW Systems, May 1, 1972. Army reply to TRW Systems questions to the IDS.

PROFILE REPORT

Lewisite (243)

1. GENERAL

Lewisite was manufactured and stored during World War II as a chemical warfare agent. The lewisite as manufactured was unstable, and most of the unused stock (about 150 tons) was destroyed by ocean dumping.

Lewisite is a lethal chemical warfare agent that acts as a vesicant, as a contact systemic poison, and as an inhalation and eye poison. Lewisite is no longer considered an important chemical warfare agent by the American military authorities, since there are now more effective chemical warfare agents with substantitally better physical and chemical properties. It is relatively easy and cheap to manufacture which may make its manufacture attractive to underdeveloped countries.

Lewisite is manufactured by adding acetylene to a mixture of arsenic (III) chloride and a catalyst of either aluminum chloride, mercuric chloride or cuprous chloride with strong agitation. The reaction temperature is maintained below 50 C. After completion of the reaction, the oily liquid product is treated with hydrochloric acid or ethanolamine hydrochloride and distilled. The lewisite product contains both the cis- and trans- forms of 2-chloroethenyl dichloroarsine.[0778]

The physical/chemical properties for the cis- and trans- forms of lewisite are summarized on the attached worksheets.

2. TOXICOLOGY

Lewisite as noted above is a skin-damaging warfare agent that acts not only as a contact poison, but also as an inhalation and eye poison. The skin-damaging effect takes place immediately. Erythemata form on the

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surface of the skin with doses of about 0.05 to 0.1 mg per square centimeter of skin surface. Concentrations of 0.2 mg per square centimeter positively lead to blister formation. Blisters on the surface of the skin are caused by gaseous lewisite after about 15 minutes dermal exposure to concentrations of 10 mg/l. Inhalalation of concentrations of 0.05 mg/l for 30 minutes or 0.5 mg/l for 5 minutes is considered lethal. An inhalation exposure of 0.05 mg/l for 15 minutes produces severe intoxication which causes a combat incapacity for several weeks. A lower concentration of 0.01 mg/l causes inflamation of the eyes and swelling of the lid after 15 minutes.[0778] British Anti-Lewisite (BAL, or dimercapto-1-propanol) is a specific antidote for lewisite contact and systematic poisoning.

3. OTHER HAZARDS

Lewisite has the power to penetrate protective materials such as leather, rubber, wood, textiles, and cause damage to the enclosed skin area.[0778]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

When stored for long periods, lewisite tends to decompose. The decomposition is accelerated by traces of acid. In the presence of iron, lewisite is catalytically converted into the secondary and tertiary arsines. However, stainless steel can usually be used with lewisite. Aluminum and aluminum alloys are corroded by lewisite. Storage of lewisite in bombs and shells is possible because stabilizers and corrosion inhibitors are used. Lewisite during storage must be protected from moisture because it is relatively easy to hydrolyze. The products of hydrolysis are hydrochloric acid and 2-chloroethenyl arsenic oxide, a poison and skin irritant.[0778]

Lewisite is shipped under Department of Transportation (DOT) regulations for a Poison, Class A. It is accepted for shipment by freight but not express.[0778]

Lewisite and lewisite contaminated wastes should be handled only by an experienced decontamination team, equipped with impermeable protective clothing, and suitable gas masks. The protective clothing should constitute a total body shield. A supply of BAL should be kept in readiness for use. Optimum procedure, if time permits, is to use Department of Defense (Army, Navy or Air Force) decontamination teams, in preference to non-governmental, civilian personnel.

No lewisite should be released to the environment and the release of arsenite compounds formed upon the treatment of lewisite should be limited. The recommended maximum concentration of arsenic compounds as arsenic discharged to streams is 1.0 ppm and the maximum recommended in drinking water is 0.05 mg/l.[0536] The recommended provisional limits for arsenic compounds for air and water are 0.005 mg/M^3 and 0.05 mg/l as As, respectively.

The safe disposal of lewisite is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis of Recommendation
Lewisite	3×10^{-6} mg/M^3	Estimate based on similar compounds

Contaminant in Water and Soil	Provisional Limit	Basis of Recommendation
Lewisite	1.5×10^{-5} ppm	Estimate based on similar compounds

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Chlorination

In dilute aqueous solution chlorine converts lewisite into arsenic trioxide and dichloroethene. Dichloroethene requires further treatment as a chlorinated organic compound.[0778] Arsenic trioxide is slightly soluble and hence should not be placed in a landfill as such. If arsenic trioxide is reacted with a suspension of magnesium hydroxide, insoluble magnesium arsenite is formed.[2345] The magnesium arsenite thus precipitated and the excess magnesium hydroxide can be stored under controlled conditions, or the slurry can be evaporated and stored in a permanent disposal area. Aqueous chlorine or sodium hypochlorite treatment, followed by reaction with magnesium hydroxide is satisfactory for decontamination or disposal of lewisite even though an arsenite is produced that must be in indefinite long term storage.

Option No. 2 - Hydrolysis

Both cis- and trans- isomers of lewisite are completely decomposed in sodium hydroxide solutions at temperatures above 40 C. The reaction proceeds as follows:

$$\text{Cl-CH= CH-AsCl}_2 \xrightarrow[H_2O]{NaOH} Na_3AsO_3 + 3NaCl + CH{=}CH\uparrow + H_2O \cdot$$ [0778]

The sodium arsenite produced is soluble and requires treatment with magnesium hydroxide, as noted above, to form insoluble magnesium arsenite before disposal in a controlled storage facility (lined lagoon, tank, abandoned quarries or mines, etc.).[2345]

Option No. 3 - Incineration (Transportable Disposal System)

The Transportable Disposal System which is described in the Profile Report on Organophosphorus Nerve Agents (287,288) can be applied to munitions or tanks containing lewisite in concentrated form. The combustion products are carbon dioxide, water, HCl and arsenic trioxide. The arsenic trioxide removed by alkaline scrubbing should be converted to the insoluble magnesium salt and placed in controlled storage.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The extreme hazards to man associated with lewisite require that surplus, scrap or obsolete lewisite and munitions containing lewisite be disposed of at National Disposal Sites operated by the U.S. Army. Options No. 1, 2 and 3 are recommended for disposal of lewisite in concentrated form, while only Option No. 3 is recommended for disposal of munitions containing lewisite.

7. REFERENCES

0536. Water quality criteria. Report of the National Technical Advisory Committee to the Secretary of the Interior. Washington, Federal Water Pollution Control Administration, Apr. 1, 1968. 234 p.

0778. Franke, S. Manual of military chemistry. Chemistry of Chemical Warfare Agents. v. 1. Washingtion. Office, Assistance Chief of Staff for Intelligence, Department of the Army, 1968. 375 p.

2345. Latimer, W. M., and J. H. Hildebrand. Reference book of inorganic chemistry. New York, the Macmillan Company, 1942. 552 p.

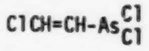
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lewisite (243)

IUC Name 2-chloroethenyl dichloroarsine
(trans and cis forms)

Common Names Lewisite; Dichloro - (2-Chlorovinyl) Arsine

Structural Formula



$ClCH{=}CH{-}As\genfrac{}{}{0pt}{}{Cl}{Cl}$

Molecular Wt. 207.32 Melting Pt. -2.4 C (trans)(1) -44.7 C (cis) Boiling Pt. 196.6 C (trans)(1) 169.8 C (cis)

Density (Condensed) 1.86 g/cc @ 25 C Density (gas) 7.15 @ 20 C

Vapor Pressure (recommended 55 C and 20 C)

0.4 torr @ 25 C (trans)(1) 1.562 @ 25 C (cis)(1) @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.5 g/l Hot Water Ethanol

Others: soluble - gasoline, most organic solvents

Acid, Base Properties

Highly Reactive with Water, base, aqueous chlorine

Compatible with

Shipped in stainless steel

ICC Classification Poison, Class A Coast Guard Classification Poison, Class A

Comments

References (1) 0778

PROFILE REPORT

Nitrogen Mustards (306)

1. GENERAL

The nitrogen mustards are chemical warfare agents stored by Germany during World War II but never applied to a combat situation. 2,2',2" trichloro triethyl amine (HN-3) can be prepared using a chlorinating agent such as thionyl chloride together with 2,2',2'' trihydroxy triethyl amine hydrochloride and reacting the product with a strong base. 2,2' dichloro diethyl methyl amine (HN-2), and 2,2' dichlorotriethyl amine (HN-1) can be prepared by analagous techniques. The nitrogen mustards and their derivatives have aquired considerable peacetime importance due to their use for cancer therapy.

2. TOXICITY[0778]

The nitrogen mustards are contact, inhalation, and eye poisons. The salts,particularly the hydrochlorides,can be used for poisoning water, foodstuffs and condiments and thus provide intoxication via the gastrointestinal tract. The liquid (as an aerosol) causes skin damage in concentrations above 0.001 mg/cm^2 of skin surface. The inhalation of nitrogen mustards causes severe respiratory difficulties. Concentrations of aerosol of 0.002 mg/l for 15 to 20 minutes leads to incapacity while concentrations of 0.25 to 1.0 mg/l have a lethal effect after brief exposure, 5 min. Slight eye damage occurs with concentrations as low as low as 0.0007 mg/l for a 15 min exposure. The lethal dose for man is between 10 and 20 mg per kilogram of body weight.

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3. OTHER HAZARDS

The low vapor pressure of these compounds limits the possible flammability and explosive hazards. Combustion of the nitrogen mustards results in the formation of the pollutants hydrogen chloride and nitrogen oxides.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Due to their toxicity the nitrogen mustards require very careful handling, protective clothing, and masks. Materials contacted by these compounds must be decontaminated actively since nitrogen mustards are slow to hydrolyze due to low solubility. A 5 percent hydrochloric or sulfuric acid solution is sufficient to form the salts which can then be washed away with large volumes of water. The water solution should be collected and dried to recover the highly toxic salts. Dry calcium hypochlorite reacts readily with the nitrogen mustards and their salts to form nonpoisonous products. This reaction, when concentrated nitrogen mustards are involved, is so violent as to cause ignition and fire hazard.

The safe disposal of nitrogen mustards is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Nitrogen Mustard (HN-1, HN-2, HN-3)	3×10^{-6} Mg/M^3	Data for similar compounds

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Nitrogen Mustard (HN-1, HN-2 & HN-3)	1.5×10^{-5} Mg/L	Data for similar compounds

Storage and Transportation

The nitrogen mustards can be stored for considerable periods in glass or steel containers if an inhibitor such as thiourea is present. The salts of the nitrogen mustards can be stored indefinitely.

No direct information on the transportation of nitrogen mustards was uncovered; however, sealed vans might be used for greater than laboratory quantities.

Disposal/Reuse

The recovery of nitrogen mustards in large quantities for military or non-military purposes is not practical due to the limited stability of the material.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Wastes

Option No. 1 - Separation. The nitrogen mustards have only slight solubility at pH values equal to or higher than 7. Thus, liquid phase separation equipment such as the centrifuge could be used for the recovery of the mustards from alkaline water media. If the nitrogen mustards have dissolved, because of an acid environment, the addition of base to neutrality or slight alkalinity will cause phase separation. The separated concentrated nitrogen mustard can be treated as described below. The effluent clarified water should for safety be treated with acidifed hypochlorite solution.

Concentrated Wastes

Option No. 1 - Incineration. (Transportable Disposal System). The transportable Disposal System which is described in the Profile Report on the Organophosphorus Nerve Agents can be applied to munitions or tanks containing the nitrogen mustards in concentrated form. The combustion products of the nitrogen mustards are carbon dioxide, water, HCl and nitrogen oxides. The nitrogen oxides require scrubbing or reduction to nitrogen and oxygen before the combustion gases are released to the atmosphere.

Option No. 2 - Chemical Reaction. The nitrogen mustards, when acidulated, react with calcium hypochlorite in solution to yield compounds with a much lower toxicity including aldehydes, chloramines, and chlorates. The reactions are violent with dry or highly concentrated hypochlorite. Care must be taken to ensure that sufficient agitation and time is allowed for the reaction due to the phase separation problem.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The hazard to man associated with vesicants such as the nitrogen mustards requires their disposal by the Army at National Disposal Sites under Army cognizance when present in munitions or when there are large quantities of the materials. The recommended techniques are summarized below:

Process	Order of Preference	Remarks
Incineration (Transportable Disposal System)	First Choice	The TDS is designed for materials of this type and is adequately safeguarded.
Chemical Reaction	Second Choice	The reaction with hypochlorite appears adequate for smaller quantities.

7. REFERENCES

0778. Franke, S., Manual of military chemistry. Chemistry of Chemical Warfare Agents. v. 1. Washingtion, Office, Assistant Chief of Staff for Intelligence, Headquarters, Department of the Army, 1968. 375 p.

2442. Departments of the Army and Air Force, Military chemistry and chemical agents. AFM 355-7. Washington, Dept. of the Army and Air Force, Dec. 1963. 101 p.

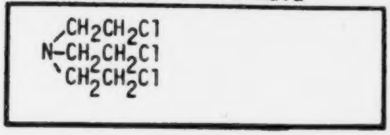
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitrogen Mustard (306)

IUC Name 2,2" dicnloro diethyl amino 2 cnloro etnane

Common Names HN-3, Nitrogen Mustard

Structural Formula



$$N\begin{cases} CH_2CH_2Cl \\ CH_2CH_2Cl \\ CH_2CH_2Cl \end{cases}$$

Molecular Wt. 204.52[2] Melting Pt. -4 C Boiling Pt. 230-235 C

Density (Condensed) 1.24 @ 20 C Density (gas) 7 Air =1.00 @

Vapor Pressure (recommended 55 C and 20 C)

.0069 mm Hg @ 20 C .009 mm Hg @ 0 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.16 g/l Hot Water Ethanol

Others: halogenated alkanes, propane, benzene, carbon disulfide, sulfur mustard, chloropicrin

Acid, Base Properties slightly basic

Highly Reactive with

Compatible with iron and steel

Shipped in

ICC Classification Coast Guard Classification

Comments Colorless and odorless, oily liquid, decomposes on heating. Thiourea used to stabilize (prevent demerization).

References (1) 0778
(2) 2442

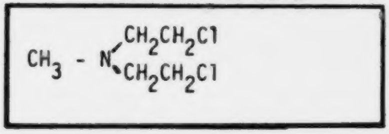
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitrogen Mustard (306)

IUC Name 2' cnloro ethyl metnyl amino 2 chloro ethane

Common Names Nitrogen Mustard, HN-2

Structural Formula



$$CH_3 - N\begin{matrix}CH_2CH_2Cl\\CH_2CH_2Cl\end{matrix}$$

Molecular Wt. 156.07 Melting Pt. -65 C Boiling Pt 75 (15 mm Hg)

Density (Condensed) 1.15 @ 20C Density (gas) 5.4 @ 20 C (air)

Vapor Pressure (recommended 55 C and 20 C)

9 mm Hg @ 71 C 0.29 @ 20 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0778

(2) 2442

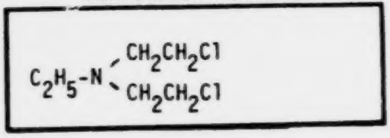
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitrogen Mustard (306)

IUC Name 2,2" dichloro diethyl amino 2 chloro ethane

Common Names Nitrogen Mustard HN-1

Structural Formula



$C_2H_5-N \begin{matrix} CH_2CH_2Cl \\ CH_2CH_2Cl \end{matrix}$

Molecular Wt. 170.8 Melting Pt. -34.4 C Boiling Pt. 85 C (10 mm Hg)

Density (Condensed) 1.0861 @ 4 C Density (gas) ______ @ ______ ______

Vapor Pressure (recommended 55 C and 20 C)

12 mm Hg @ 85.5 C 0.25 mm Hg @ 25 C ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water ______ Hot Water ______ Ethanol ______

Others: ______

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification ______ Coast Guard Classification ______

Comments ______

References (1) 0778

(2) 2442

PROFILE REPORT

Sulfur Mustard (543)

1. GENERAL

Sulfur mustard, bis(2-chloroethylene) sulfide, is a heavy, oily liquid. It has very little odor in the pure state, but the technical material smells strongly of mustard or horseradish. There are three types of technical mustard: H, HD and HT. H is the symbol for mustard made by the Levinstein process and contains up to 25 percent impurities by weight. The impurities are chiefly sulfur, organo-sulfur-chlorides, and polysulfides. HD is mustard that has been purified by washing and vacuum distillation. HT mustard is a mixture of 60 percent HD and 40 percent bis-beta chloroethyl thioethyl ether, $(ClC_2H_4SC_2H_4)O$, formulated to lower the freezing point to 32 F.

Technical mustard is manufactured by the Levinstein process which consists of bubbling dry ethylene into sulfur monochloride at approximately 35 C. Some mustard from a previous batch is usually left in the reactor. The simplified reaction is

$$S_2Cl_2 + 2CH_2{:}\ CH_2 \rightarrow (ClCH_2CH_2)_2S + S$$

After the mustard is made it is allowed to settle for a while to permit some of the impurities to settle out. The resultant material is a light brownish material.

The physical/chemical properties for bis(2-chloroethyl) sulfide are summarized on the attached worksheet.

2. TOXICOLOGY

Sulfur mustard is a persistent and powerful blister agent. Both liquid and vapor cause intense inflammation which may blister the skin or mucous membrane with which they come in contact. Mustard acts first as a cell irritant and finally as a cell poison on all tissue surfaces contacted. The first symptoms of mustard poisoning usually appear in four to six hours. The higher the concentration, the shorter the interval of time between exposure and the first symptoms. The physiological action is both local and general. Exposure results in conjunctivitis, erythema followed by blistering and ulceration, and inflammation of the nose, throat, trachea, bronchi and lung tissue.[0778,0952] The effects of sulfur mustard vapors as functions of time and concentration are summarized below:[2442]

Median lethal dosage

Inhalation	1,500 mg-min/m^3
Skin absorption (masked personnel)	10,000 mg-min/m^3

Median incapacitating dosage

Eye injury	200 mg-min/m^3
Skin absorption (masked personnel)	2,000 mg-min/m^3

Elevated temperatures and high humidity increase the casuality effect of HD. Slight eye injury can result from dosages as low as 50 to 75 mg-min/m^3. Susceptibility varies with individuals. Injuries produced by mustard heal more slowly than thermal burns, and are more liable to infection. The rate of detoxification is very low. Even very small repeated exposures are cumulative in their effects, or are more than cumulative due to sensitization.[2442]

Sulfur mustard is readily absorbed by rubber and leather. When working with mustard special protective clothing and ointments are required.

Sulfur mustard and mustard contaminated wastes should be handled only by an experienced decontamination team, equipped with impermeable protective clothing and air supplied gas masks. The protective clothing should constitute a total body shield.

The American Conference of Governmental Industrial Hygienists (ACGIH) has not established a Threshold Limit Value (TLV) for sulfur mustard but a maximum allowable concentration of 5×10^{-2} ppb has been recommended for an 8-hr working day.[0225,0778]

The saturation concentration for sulfur mustard is 0.6 mg per liter. This indicates that it will have a good persistency, in fact it is the most persistent of the usable chemical warfare agents.[0778,0952] Heavily splashed liquid persists 1 to 2 days under average weather conditions, and a week or more under very cold conditions.[2442]

Decontaminants employed to counteract the effects of mustard include bleach, M5 ointment, fire, or DS2 (70 percent diethylenetriamine, 28 percent ethyleneglycolmonomethyl ether, and 2 percent NaOH).

3. OTHER HAZARDS

Impure sulfur mustard usually contains water and hydrochloric acid which has a corrosive effect on iron and steel. The iron salts formed promote continued corrosion. In addition, decomposition products from the mustard form hydrogen, hydrogen sulfide, and acetylene. A pressure rise is possible in closed containers, shells, bombs, and transportation containers. Corrosion inhibitors and antioxidation agents are usually added to sulfur mustard.[0778]

Sulfur mustard is shipped under Department of Transportation (DOT) regulations for a Poison, Class A. It is accepted for shipment by freight but not express.[0776]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The safe disposal of sulfur mustard is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant In Air	Provisional Limit	Basis for Recommendation
Sulfur mustard	3×10^{-6} mg/M^{3}*	0.01 TLV*

Contaminant In Water and Soil	Provisional Limit	Basis for Recommendation
Sulfur mustard	1.5×10^{-5} mg/l*	Stokinger and Woodward method*

Virtually all of the sulfur mustard wastes are contained in obsolete chemical munitions scheduled for disposal.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Chlorination

Sulfur mustard added to 10 percent calcium hypochlorite solution is decomposed according to the following equation:

$$S(CH_2CH_2Cl)_2 + 7\ Ca(OCl)_2 + 2\ Ca(OH)_2 \rightarrow CaSO_4 + 8\ CaCl_2 + 4CO_2 + 6H_2O$$

Thus 7.0 lb of $Ca(OCl)_2$, which contains 0.7 lb of CaO equivalent to 0.93 lb of $Ca(OH)_2$, are theoretically required to detoxify one lb of sulfur mustard. Some mustard sulfone may be formed in accordance with the following reaction:

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*Estimated from data for similar compounds.

$$2CaCl(OCl) + (ClCH_2CH_2)_2S \rightarrow 2CaCl_2 + (ClCH_2CH_2)_2SO_2$$

Mustard sulfone produces severe burns if left on the skin. In practice, therefore, 1.2 times the required amount of $Ca(OCl)_2$ is used. The decontamination is conducted in a closed system where all air leaving the system is scrubbed through $Ca(OCl)_2$ solution and filtered. The salts formed upon detoxification are placed in a landfill after evaporation of the water.[0778] This treatment process is used to treat sulfur mustard that is excess, contaminated or loaded in surplus munitions.

Option No. 2 - Incineration (Transportable Disposal Site)

The Transportable Disposal System which is described in the Profile Report on Organophosphorus Nerve Agents (287,288) can be applied to munitions or tanks containing sulfur mustard in concentrated form. The sulfur mustard may be dissolved in gasoline and the gasoline solution incinerated. The combustion products will be carbon dioxide, water, sulfur oxides, and hydrogen chloride which are removed by alkaline scrubbing.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The extreme hazards to man associated with sulfur mustard require that surplus, scrap, or obsolete sulfur mustard and munitions containing sulfur mustard be disposed of at National Disposal Sites operated by the U.S. Army. Option No. 2 is recommended for disposal of sulfur mustard in concentrated form or for disposal of sulfur mustard in munitions.

7. REFERENCES

0225. American Conference of Governmental Industrial Hygienists. Threshold Limits for 1971. Occupational Hazards, Aug. 1771. p. 35-40.

0766. Sax, N. I. Dangerous properties of industrial materials. 2d. ed. New York, Reinhold Publishing Corporation, 1957. 1,467 p.

0778. Franke, S. Manual of military chemistry. Chemistry of Chemical Warfare Agents. v. 1. Washington. Office, Assistant Chief of Staff for Intelligence, Department of the Army, 1968. 375 p.

0952. U.S. Army. Demilitarization of toxic munitions at U.S. Army Material Command installations, Environmental Statement PB 203-509. Edgewater Arsenal, Maryland, Department of the Army Headquarters, Edgewater Arsenal, 1971.

2442. Department of the Army Technical Manual TM3-215/Department of the Air Force Manual AFM 3557. Military Chemistry and Chemical Agents. Departments of the Army and the Air Force, Washington. December 1963 101 p. (Changes C1 and C2, 16 March 1965 and 15 June 1967).

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sulfur Mustard (543)

IUC Name 2,2' dichlorodiethylsulfide

Common Names H, HD

Structural Formula

$(ClCH_2CH_2)_2S$

Molecular Wt. 159.08(3) Melting Pt. 13.5 C(1) Boiling Pt. 227.8 C(3)

Density (Condensed) 1.2741g/cc @ 200(1) Density (gas) 5.4(air) @ 20 C(3)

Vapor Pressure (recommended 55 C and 20 C)

0.05 torr @ 10 C(1) 0.1 torr @ 20 C(1) 0.2 torr @ 30 C(1)

Flash Point 105 C(3) Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.8g/l at 20 C(1) Hot Water Ethanol absolute(1) miscible

Others:

Acid, Base Properties

Highly Reactive with oxidizing agents(1)

Compatible with Most metals if acid impurities are absent(1)

Shipped in Steel or aluminum containers

ICC Classification Poison, Class A(2) Coast Guard Classification Poison, Class A(2)

Comments Decomposition temperature 149 to 177 C(3)

References (1) 0778
(2) 0776
(3) 2442

PROFILE REPORT

Tear Gas, Irritant (CS) (423)

1. GENERAL

Irritant tear gas (CS) or 2-chlorobenzylidene malononitrile is employed as a riot control agent. As an aerosol it is a powerful irritant to the eyes and upper respiratory organs. CS is a white crystalline substance that is prepared by reacting 2-chlorobenzaldehyde with malonic acid nitrile.[0778]

The physical/chemical properties of CS are summarized in the attached worksheet.

2. TOXICOLOGY

Individuals exposed to CS develop a severe conjunctivitis which is accompanied by a burning sensation, great pain, and a flow of tears. With the exception of the conjunctivitis, the effects last only 5 to 15 minutes. The intensity of conjunctivitis decreases after 25 to 30 minutes. Other symptoms of CS intoxication are copious nasal discharge and flow of saliva, as well as irritation of the nose. Headache, nausea and lethargy are non-specific and do not occur in all cases. With longer exposure or high concentrations, erythemata and blisters develop.

The Threshold Limit Value (TLV) for tear gas is 0.4 mg/M^3.[0225] The maximum exposure time that various concentrations can be tolerated are listed below[0778]:

Exposure Time	Maximum Concentration
1 minute	5 mg/M^3
12 seconds	10 mg/M^3
6-9 seconds	34 mg/M^3
Incapacity to minimum function	1-5 mg/M^3

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3. OTHER HAZARDS

When CS is exposed to moisture, hydrolysis takes place. The products of hydrolysis are 2-chlorobenzaldehyde and malonic acid nitrile, a highly toxic material.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Personnel handling, manufacturing, using or disposing of CS must have available gas masks of a design approved by U.S. Bureau of Mines for CS service with approved cannisters for CS. All equipment must be adequately designed to prevent release of CS to the atmosphere. CS is shipped under Department of Transportation (DOT) regulation for a Poison, Class C.[0766] The safe disposal of CS is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
CS	0.004 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
CS	0.020 mg/l	Estimated by analogy to chlorpicrin and chloracetophenone

Information furnished to TRW by the California Department of Justice, and a major riot control device manufacturer, indicates that there are no local government waste disposal requirements for overage and obsolete riot control devices/agents. Governmental law enforcement agencies (local) use all of the overage or obsolete devices for training exercises. There are some stocks of riot control agents at Federal (Defense) storage points scheduled for disposal. The quantities and locations of these agents and their waste forms are given in Volume XIV of this Final Report, under the heading "Chemical and Riot Control Agents".

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processes for treatment of CS waste are briefly described in the following paragraphs. The processes described are for handling concentrated CS, but these methods with slight modification can be used to decontaminate an area contaminated with CS.

Option No. 1 - Hydrolysis Followed by Incineration

CS is relatively resistant to hydrolysis by pure water. However, in a 95 percent ethanol and 5 percent water solution at 30 C, 99 percent of the CS present is hydrolyzed. CS waste may be treated by dissolving the material in 95 percent enthanol, allowing the mixture to stand overnight, and then destroying the hydrolysis products and residual CS by incineration followed by a caustic scrubber. The products of hydrolsis are 2-chlorobenzaldehyde and malonic acid nitrile. This technique is acceptable for treatment of small quantities of CS.

Option No. 3 - Hypochlorite Treatment

Oxidizing agents attack the ethylenic linkage in the side chain to form various products. If hypochlorite is used in an aqueous solution with CS, an epoxide is formed at the double bond.[0778] The treatment of CS with a hypochlorite solution will detoxify the CS, but a new material is formed which requires disposal. Except for decontamination operations, this process is not recommended.

Option No. 3 - Chemical Agent Munition Disposal System

The former Transportable Disposal System (now known as the Chemical Agent Munition Disposal System) described in the Profile Report on the Nerve Gases (27,28) is well suited to the disposal of munitions containing riot-control agents. When the Army Materiel Command has completed development of this automated, scrubber equipped incineration system, the technique will be the preferred method of disposal for CS containing military ordnance items.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Military ordnance materiel classified as surplus which contains, CS should be disposed of by the Army at National Disposal Sites under Army Cognizance, by the technique of Option No. 3 above.

7. REFERENCES

0225. American Conference of Government Industrial Hygienist. Threshold Limit Values for 1971. Occupational Hazards, Aug. 1971. p. 35-40.

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed., New York, Reinhold Publishing Corp. 1968. 1,251 p.

0778. Franke, Siegfried. Manual of military chemistry, chemistry of chemical warfare agents, V 1. Deutscher Militarverlag, 1967, East Berlin. Translated by Assistant Chief of Staff for Intelligence, Department of the Army, AD849866, Washington. 1968. 542 p.

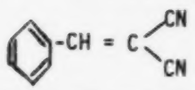
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tear gas, irritant(CS) (423)

IUC Name 2-chlorobenzylidene malononitrile

Common Names Tear gas

Structural Formula



Molecular Wt. 153 (1) Melting Pt. 95 C (1) Boiling Pt. 310 to 315 C (1)

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water soluble (1) Hot Water soluble (1) Ethanol soluble (1)

Others: soluble - gasoline, acetone (1)

Acid, Base Properties

Highly Reactive with Oxidizing agents (1)

Compatible with

Shipped in

ICC Classification Poison, Class C (1) Coast Guard Classification Poison, Class C (1)

Comments

References (1) 0778